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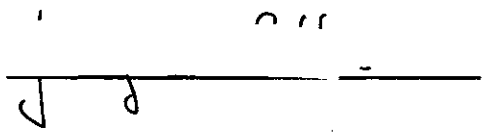

THEORETICAL STUDIES OF
ELECTRONIC STATES OF SIMPLE POLYATOMIC MOLECULES

Part I. Gaussian Expansion of Wavefunctions

Part II. Magnetic Interactions in the Triplet State of Glyoxal

A THESIS

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The Faculty of the Graduate Division

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SUMMARY

A new method of using Gaussian functions of the form $\exp(-ar^2)$ in the construction of electronic wavefunctions for molecules is suggested. The formulation is shown to be of considerable utility both in conventional molecular energy calculations, and in the evaluation of electronic properties in general. Hydrogen-like atomic orbitals are expanded as linear combinations of Gaussian functions, but without the use of angular variables θ and φ. The angular dependence in p and d atomic orbitals is achieved by judiciously locating $\exp(-ar^2)$ functions at different points in space determined in part by orbital symmetry.

The Gaussian function formulation is used in electronic energy calculations of H_2^+, H_2, He, N, and N_2, and in the evaluation of spin-spin and spin-orbit interactions in glyoxal. Orbital angular momentum and quadrupole moment integrals are also evaluated.

A novel treatment of the hydrogen molecule ion is reported in which a wavefunction is constructed as a linear combination of exponential basis functions centered at the nuclei, plus an exponential or Gaussian function centered in the bond region midway between the nuclei. The addition of a center function gives a calculated dissociation energy in close agreement with the experimental value, but unlike other successful treatments of H_2^+, the formulation is extendible to larger systems. The use of a center function in the hydrogen

molecule wavefunction does not significantly improve the calculated dissociation energy. However, the error is attributable to a lack of angular electron correlation, and is not due to a failure of the one electron description.

A detailed treatment of magnetic interactions in the triplet state of glyoxal, ^3A_u, is given based on Van Vleck's general theory of coupling of angular momenta in molecules. Explicit formulas for coupling constants which are not given by Van Vleck are derived. The results of the treatment predict the magnitude of splitting of the symmetric rotor energy levels caused by interactions involving electron spin. All integrals over electronic wavefunctions are evaluated using Gaussian function expansions of atomic orbitals.

An estimate of the singlet-triplet transition probability in glyoxal is determined by taking into account the mixing of singlet and triplet wavefunctions caused by spin-orbit interactions. In addition, the probability of a transition from the ground state, ^1A_g, to the excited singlet state, ^1B_g, by a magnetic dipole mechanism is calculated.

The splitting of the triplet state energy levels of glyoxal in the presence of an external magnetic field is discussed, and comments are made concerning the nature of a magnetic rotation spectrum.

PART I

GAUSSIAN EXPANSION OF WAVEFUNCTIONS

CHAPTER I

THREE CENTER BASIS FUNCTIONS FOR THE HYDROGEN MOLECULE AND MOLECULE ION

Introduction

The hydrogen molecule and molecule ion are of distinctive theoretical importance as prototypes of chemically bonded systems, in which H_2^+ exemplifies multinuclear attraction of an electron, and H_2 introduces the additional problem of electron interaction. Both molecules have been solved by accurate quantum mechanical treatments (1-4), but the methods of solution are not easily extended to other molecules. Consequently, many approximate treatments have been proposed in efforts to find a reasonably accurate formulation that would be applicable to larger systems (5,6).

Different formulations are conveniently compared on the basis of a total molecular energy calculation, and subsequent determination of the experimentally observable dissociation energy. The variational theorem of calculus provides the inequality,

$$E_{exact} \leq \langle \psi | T+V | \psi \rangle$$

between the exact energy eigenvalue and the calculated total energy expectation value, kinetic energy plus potential energy, corresponding to an approximate wavefunction, ψ, for the system. Furthermore, as expectation values converge to the exact eigenvalue, approximate

wavefunctions converge in the mean to the exact wavefunction; thus, a calculated expectation value close to the exact value justifies some confidence in the approximate wavefunction, but as is well known, the energy is not as sensitive to the wavefunction as certain other molecular properties.

The only formulation that has been applied extensively to larger molecules is the method of constructing wavefunctions as linear combinations of atomic orbitals. Thus, for H_2^+ a simple one electron function is

$$\psi = N^{-1}\{S_A + S_B\}$$

where S_A and S_B are 1s hydrogen-like orbitals, $Z^{\frac{3}{2}}\pi^{-\frac{1}{2}}\exp(-Zr)$, with origins at the nuclei A and B. Historically (7), the energy was minimized simply by treating Z as a variational parameter to give

$$E = -15.85 \text{ ev.}$$
$$D^e = 2.25 \text{ ev.}$$
$$Z = 1.228$$

Actually, the variation in Z has the more subtle consequence of bringing the calculation into agreement with the virial theorem. The theorem, which is applicable in both classical and quantum mechanics, requires that the following condition be satisfied for an equilibrium configuration of nuclei and a potential function derivable from inverse square forces,

$$\langle\psi|T|\psi\rangle = -\tfrac{1}{2}\langle\psi|V|\psi\rangle = -\langle\psi|T+V|\psi\rangle$$

Without a variation of Z in the H_2^+ function the equalities are not satisfied.

A useful technique for scaling wavefunctions in order to satisfy the virial theorem automatically was introduced by Hylleraas and later emphasized by Löwdin and Slater (8-10). The technique involves an extraction of the scale factor, Z, from kinetic and potential energy integrals to give the energy expression

$$E = Z^2\langle\psi|T|\psi\rangle + Z\langle\psi|V|\psi\rangle = -\frac{\langle\psi|V|\psi\rangle^2}{4\langle\psi|T|\psi\rangle}$$

which is then minimized with respect to the scaled internuclear distance, ZR. Knowledge of the kinetic and potential energies corresponding to the minimum total energy permits an automatic determination of Z as,

$$Z = -\frac{\langle\psi|V|\psi\rangle}{2\langle\psi|T|\psi\rangle}$$

An extension of the LCAO technique to the hydrogen molecule requires construction of a not so obvious two electron wavefunction. The simplest choice is a product of the one electron wavefunctions for H_2^+,

$$\Psi(1,2) = \psi(1)\psi(2)$$

and thus corresponds to a superposition of individual electron densities. A dissociation energy of $D^e = 3.47$ ev. compared with the experimental value 4.72 ev. is obtained for the best choice of Z (11). A slightly

more elaborate function, used by Weinbaum (11), in which the previous electron distribution is modified in order to reduce electron repulsion is

$$\Psi(1,2) = N^{-1}\left\{\psi(1)\psi(2) - \lambda\left[S_A(1)S_A(2) + S_B(1)S_B(2) - S_A(1)S_B(2) - S_A(2)S_B(1)\right]\right\}$$

where λ is now another variational parameter and S_A and S_B are 1s hydrogen-like orbitals. The additional term has the significance of removing some of the ionic character $S_A(1)S_A(2)$ and $S_B(1)S_B(2)$, or alternatively, of partly correlating electrons to opposite ends of the molecule. The dissociation energy is improved to 4.00 ev., and as such is about the best value obtainable by a simple treatment.

Other functions superior to the LCAO function for H_2^+ have been applied to H_2, but without exception, good H_2^+ functions are not extendible to molecules other than H_2. A notable example is the James function (12),

$$\psi = N^{-1}(1+b\nu^2)\, e^{-a\mu}$$

where μ and ν are the elliptical coordinates

$$\mu = (r_A + r_B)R^{-1}$$

$$\nu = (r_A - r_B)R^{-1}$$

and a and b are variational parameters. A very good H_2^+ dissociation energy of 2.772 ev. compared with the exact value, $D^e = 2.7773$ ev., is obtained (12); however, the elliptical coordinate formulation is not readily extended to larger molecules.

One of the purposes of this work is to obtain a good wavefunction for H_2^+, applicable in general to other molecules. Any subsequent errors that occur in an application to H_2 would then be attributed to inadequate electron correlation, and not to any inherent error in the one electron description. To this effect, a simple three term linear combination employing a function centered midway between the nuclei is suggested for H_2^+, and is applied in a configuration interaction treatment of H_2. A much improved dissociation energy is obtained for H_2^+; but the application to H_2 indicates inadequacies which appear correctable only by including angular electron correlation or by the explicit introduction of the interelectronic distance into the wavefunction.

Hydrogen Molecule Ion

The hydrogen molecule ion wavefunction was written as the linear combination,

$$\psi = N^{-1}\{S_A + \gamma S_B + S_C\}$$

The functions S_A and S_C are centered at the nuclei; S_B is centered midway between the nuclei. Two choices of functions were made. In the first case, all three functions were chosen as 1s orbitals with equal scale factors. Thus,

$$\psi = N^{-1}\{\exp(-ar_A) + \gamma \exp(-ar_B) + \exp(-ar_C)\}$$

where r_A and r_C are radial coordinates from the nuclei A and C, and r_B is the radial coordinate from a point midway between the nuclei.

In the second choice, exponential functions were used at the nuclei, but the center function was replaced by a Gaussian function, $\exp(-br_B^2)$.

The energy integral,

$$\langle \psi \left| -\tfrac{1}{2}\nabla^2 - \frac{1}{r_A} - \frac{1}{r_C} + \frac{1}{R_{AC}} \right| \psi \rangle$$

in atomic units, was minimized by a complete variation of all parameters including the internuclear distance R_{AC}. Formulas for the required integrals which were derived using elliptical coordinates are given in Appendix I. In actual calculations the scaling technique was employed by fixing $a = 1$ and minimizing

$$E = \frac{-\langle \psi | V | \psi \rangle^2}{4\langle \psi | T | \psi \rangle}$$

with respect to R_{AC}, and also b, in the case of a Gaussian center function. The best scale factor is then

$$a = -\frac{\langle \psi | V | \psi \rangle}{2\langle \psi | T | \psi \rangle}$$

corresponding to expectation values evaluated at the minimum energy, and

$$\psi = N^{-1}\{\exp(-ar_A) + \gamma \exp(-a^2 b r_B^2) + \exp(-ar_C)\}$$

The scaled kinetic energy is

$$a^2 \langle \psi | T | \psi \rangle$$

and the scaled potential energy

$$a \langle \psi | V | \psi \rangle$$

corresponding to a total energy

$$E = a^2\langle\psi|T|\psi\rangle + a\langle\psi|V|\psi\rangle = -\frac{\langle\psi|V|\psi\rangle^2}{4\langle\psi|T|\psi\rangle}$$

Results are given in Table 1. The dissociation energy was improved to 2.644 ev. with an exponential center function and to 2.763 ev. with a Gaussian center function, compared with the exact value, $D^e = 2.7773$ ev.

Hydrogen Molecule

Several two electron wavefunctions were constructed for the hydrogen molecule using four configurations with a three center molecular orbital. Exponential functions with equal scale factors were located at each nucleus, and also at a point midway between the nuclei. The choice of equal scale factors is not necessarily the best choice, but is one that simplifies evaluation of the three center electron repulsion integrals. Formulas for all required integrals are given in Appendix I. The Gaussian center function was used in only one calculation in which the exponential functions were replaced by Gaussian function expansions.*

The energy integral,

$$\langle\Psi(1,2)\left|\sum_{k=1}^{2}\left(-\tfrac{1}{2}\nabla_k^2 - \frac{1}{r_{Ak}} - \frac{1}{r_{Ck}}\right) + \frac{1}{R_{AC}} + \frac{1}{r_{12}}\right|\Psi(1,2)\rangle$$

was minimized for each wavefunction by variation of all parameters, including the internuclear distance R_{AC}, using the same scaling procedure as in the molecule ion treatment. Results are given in Table 2.

*The Gaussian function formulation is discussed in Chapter IV.

Table 1. Hydrogen Molecule Ion

Wavefunction[a]	Total Energy[b] (a.u.)	D_e (ev.)
1. Recalculation using the Finkelstein and Horowitz Function[c] $\psi = N^{-1}\{\exp(-a r_A) + \exp(-a r_C)\}$ $a = 1.238$, $R_{AC} = 2.003$ a.u.	-0.58651	2.354
2. Exponential Center Function $\psi = N^{-1}\{\exp(-a r_A) + \gamma \exp(-a r_B) + \exp(-a r_C)\}$ $a = 1.28$, $\gamma = 0.3557$, $R_{AC} = 2.00$ a.u.	-0.59720	2.644
3. Gaussian Center Function $\psi = N^{-1}\{\exp(-a r_A) + \gamma \exp(-b r_B^2) + \exp(-a r_C)\}$ $a = 1.2539$, $b = 0.51889$, $\gamma = 0.275$, $R_{AC} = 2.006$ a.u.	-0.60157	2.763
4. James Function (12) $\psi = N^{-1}(1 + b\nu^2) \exp(-a\mu)$ $\mu = R^{-1}(r_A + r_C)$, $\nu = R^{-1}(r_A - r_C)$, $a = 1.35$, $b = 0.448$	-0.6024	2.772
5. Exact Numerical Solution (1-3)	-0.60262	2.7773

a. Basis functions are centered at the nuclei A and C, and midway between the nuclei at B.

b. One atomic unit equals 27.206 ev., 0.529 Å.

c. A careful minimization of the Finkelstein and Horowitz energy expression gives -0.58651 a.u. instead of the reported value 0.583 a.u.

Table 2. Hydrogen Molecule

	Wavefunction[a]	Total Energy (a.u.)	D^e (ev.)
1.	One Configuration Function[a] $\psi = \psi_1(1)\ \psi_1(2)$ $\gamma = 0.18$, $a = 1.195$, $R_{AC} = 1.389$ a.u.	-1.13079	3.558
2.	Two Configuration Function $\psi = N^{-1}\{\psi_1(1)\ \psi_1(2) + \ell\ \psi_2(1)\ \psi_2(2)\}$ $\gamma = 0.15$, $a = 1.189$, $\ell = -0.140$, $R_{AC} = 1.43$ a.u.	-1.14858	4.042
3.	Three Configuration Function $\psi = N^{-1}\{\psi_1(1)\ \psi_1(2) + \ell\ \psi_2(1)\ \psi_2(2)$ $+ m(\psi_1(1)\ \psi_3(2) + \psi_3(1)\ \psi_1(2)\}$ $\gamma = 2.3$, $a = 1.195$, $\ell = -0.1165$, $m = 0.158$, $R_{AC} = 1.43$ a.u.	-1.15020	4.086
4.	Four Configuration Function $\psi = N^{-1}\{\psi_1(1)\ \psi_1(2) + \ell\ \psi_2(1)\ \psi_2(2)$ $+ m(\psi_1(1)\ \psi_3(2) + \psi_3(1)\ \psi_1(2)) + n\ \psi_3(1)\ \psi_3(2)\}$ $\gamma = 2.3$, $a = 1.195$, $\ell = -0.1158$, $m = 0.1468$, $n = 0.00081$, $R_{AC} = 1.43$ a.u.	-1.15068	4.099
5.	Weinbaum Function (11)	-1.1515	4.10
6.	James and Coolidge Solution (4)	-1.1735	4.721
7.	Experimental (13)		4.74

a. Normalized molecular orbitals are defined as follows:
$\psi_1 = N^{-1}(S_A + \gamma S_B + S_C)$, $\psi_2 = N^{-1}(S_A - S_C)$, $\psi_3 = N^{-1}(S_A - \delta S_B + S_C)$
where S_A, S_B, and S_C are exponential functions, $a^{3/2}\ \pi^{-1/2}$ $\exp(-ar)$, centered at the nuclei A and C, and at a point B midway between the nuclei. The constant δ is chosen so that ψ_3 is orthogonal to ψ_1.

The best calculated dissociation energy is essentially the same as the 4.10 ev. value obtained by Weinbaum using 1s and 2p basis functions centered at the nuclei (11), and likewise the one configuration result is only slightly better than the simple (scaled) LCAO value of 3.47 ev.

Conclusion

The relative success of the three center basis description of H_2^+, and the subsequent failure in H_2, is clearly significant. In H_2^+, the addition of a center function provides a needed increase in electron density in the bond region, thus giving a much improved wavefunction for an electron in the field of two nuclei. The dissociation energy of the best three-center wavefunction compares favorably with the James function result given in Table 1.

The situation in H_2 is different. Electron repulsion apparently makes it undesirable to favor the central region by the addition of a center function. Additional configurations that are obtained by adding such a function are all axially symmetric, and hence can modify only the axial correlation of electrons. This seems to be insufficient to improve the bonding energy. Thus, there is obtained further confirmation of Shull's contention that any significant improvement in the H_2 dissociation energy over approximately 4.24 ev. can only come from an introduction of angular correlation.

CHAPTER II

GAUSSIAN EXPANSION OF HYDROGEN ATOM WAVEFUNCTIONS

Introduction

The importance of Gaussian functions, characterized by a squared distance in the exponential, $\exp(-ar^2)$, in the representation of electronic wavefunctions has been slow to gain recognition since establishment of the basic theory in 1950 (15-25). Impetus to the use of Gaussian functions is still largely because of a default of hydrogen-like functions. The latter are the logical electronic functions since they are solutions to the problem of an electron in the field of one nucleus; but associated computational difficulties have not been solved, nor is there currently any great hope for solution except in two-center problems (24).

Gaussian functions, in contrast, have the special advantage that all multicenter overlap, kinetic energy, nuclear potential and electron repulsion integrals are easily evaluated (15). This advantage is offset by the fact that Gaussian functions, by themselves, are rather inferior approximations to wavefunctions since the functions do not have the correct behavior near the nucleus, neither do they behave correctly at large distances from the nucleus.

There are, however, three ways in which Gaussian functions may be used to advantage in molecular calculations. In the first method, a many-electron wavefunction is expanded directly in terms of a complete

set of Gaussian radial functions and the spherical harmonic angular functions. This approach is exemplified by Meckler's configuration interaction treatment of the oxygen molecule (22).

A second method involves expansion of hydrogen-like, Slater or self-consistent-field functions in terms of Gaussian functions (21). Spherical harmonic functions are retained as angular parts. Problems are then formulated in terms of the conventional orbitals, but computations are made with Gaussian function expansions. McWeeny (16, 17) has obtained rough approximations for 1s, 2s, and 2p functions using two term sums of the form $\exp(-ar^2)$, $x\cdot\exp(-ar^2)$, and $r^2\exp(-ar^2)$ with variable exponent a. The resulting functions were used to approximate bond-scattering factors for x-rays. More accurate expansions have since been obtained by using a larger number of terms (23).

Both of the above methods give rise to integrals involving products of Gaussian functions with spherical harmonics. These integrals may be derived from the general formulas of Boys (15) by differentiation with respect to appropriate parameters, but in multicenter problems, the use of spherical harmonics introduces some computational difficulty.

A third use of Gaussian functions is suggested in this thesis in which hydrogen-atom wavefunctions are expanded without angular variables, using only functions of the form $\exp(-ar^2)$. The angular dependence in p and d atomic orbitals is achieved by centering the $\exp(-ar^2)$ functions at different points in space, not at the nucleus. Approximations appear to be sufficiently accurate to find use in molecular energy calculations, and the computational difficulties associated with spherical harmonics are obviated (25).

Expansion of Wavefunctions

The hydrogen atom orbitals 1s, 2s, 2p, and 3d with the exception of the $3d_{z^2}$ orbital are expanded as linear combinations of Gaussian functions where individual functions are located at points in space determined in part by the symmetry of the orbital to be expanded. Thus, a function φ which is to approximate an exact orbital is written as the sum of Gaussian functions with origin at point j in space and variable exponent a_j,

$$\varphi = N^{-1} \sum_{j=1}^{n} c_j e^{-a_j r_j^2}$$

Each linear combination is normalized and orthogonalized with lower approximate eigenfunctions. The energy integral for the hydrogen atom,

$$\langle \varphi | -\tfrac{1}{2}\nabla^2 - \tfrac{1}{r} | \varphi \rangle$$

in atomic units, is minimized by variation of all parameters using the scaling technique discussed in Chapter I. The virial theorem, therefore, is satisfied automatically.

As the calculated energy eigenvalue approaches the exact eigenvalue, the trial wavefunction converges in the mean toward the exact eigenfunction. This is equivalent to convergence to an overlap integral of unity between exact and approximate eigenfunctions.

In the 1s expansion, all Gaussian functions are located at the nucleus. The results of successive approximations are given in Table 3,

Table 3. Expansion of 1s Function

	Function	Energy, a.u. *
1.	$(2a/\pi)^{3/4}\ e^{-ar^2}$ $a = 0.28294$	-0.42441
2.	$N^{-1}\{(2a/\pi)^{3/4}\ e^{-ar^2} + 3.0(2b/\pi)^{3/4}\ e^{-br^2}\}$ $a = 1.3414,\ b = 0.20121,\ N = 3.64921$	-0.485809
3.	$N^{-1}\{(2a/\pi)^{3/4}\ e^{-ar^2} + 5.721\ (2b/\pi)^{3/4}\ e^{-br^2} + 9.03(2c/\pi)^{3/4}\ e^{-cr^2}\}$ $a = 4.4511,\ b = 0.6766,\ c = 0.1509,\ N = 13.9858$	-0.496979
4.	$N^{-1}\{(2a/\pi)^{3/4}\ e^{-ar^2} + 4.90(2b/\pi)^{3/4}\ e^{-br^2} + 6.70(2c/\pi)^{3/4}\ e^{-cr^2} + 0.156(2d/\pi)^{3/4}\ e^{-dr^2}\}$ $a = 2.83994,\ b = 0.578897,\ c = 0.139452,\ d = 17.4990,$ $N = 11.26155$	-0.49901
5.	Exact: $\pi^{-1/2}\ e^{-r}$	-0.5000

*1 a.u. = 27.206 e.v.

and a graph of the exact function and the best approximation is given in Figure 1. The calculated overlap of the four term approximation with the exact function is 0.99969. The two term function given in the table agrees with McWeeny's (17).

The 2s orbital, $(32\pi)^{-1/2}\,(2 - r)e^{-r/2}$, is expanded as a linear combination of three Gaussian functions centered at the nucleus, orthogonalized to either the three- or four-term 1s approximation. The two expansions are given in Table 4. A radial plot of the 2s approximation is not shown, but the fit to the exact function is comparable to that obtained in the 1s case. The Slater 2s function, $r\,e^{-r/2}$, may be obtained from the above 2s functions by solving for $r\,e^{-r/2}$ and replacing $e^{-r/2}$ by the 1s expansion with a scale factor 1/2.

The $2p_z$ orbital, $(32\pi)^{-1/2}\,r\cos\theta\,e^{-r/2}$, is expanded as the difference between two lobe functions φ_1 and φ_2 which are identical linear combinations of Gaussian functions except that Gaussian functions belonging to φ_1 have point 1 in Figure 2 as the origin, while φ_2 functions have origin at point 2. Thus,

$$\Phi_{2p_z} = N^{-1}\{\Phi_1 - \Phi_2\}$$

where

$$\Phi_1 = \sum_{k=1}^{n} c_k e^{-a_k r_1^2} \qquad \Phi_2 = \sum_{k=1}^{n} c_k e^{-a_k r_2^2}$$

and r_1 and r_2 are radial coordinates from points 1 and 2 respectively. Results of successive approximations are given in Table 5 where there is

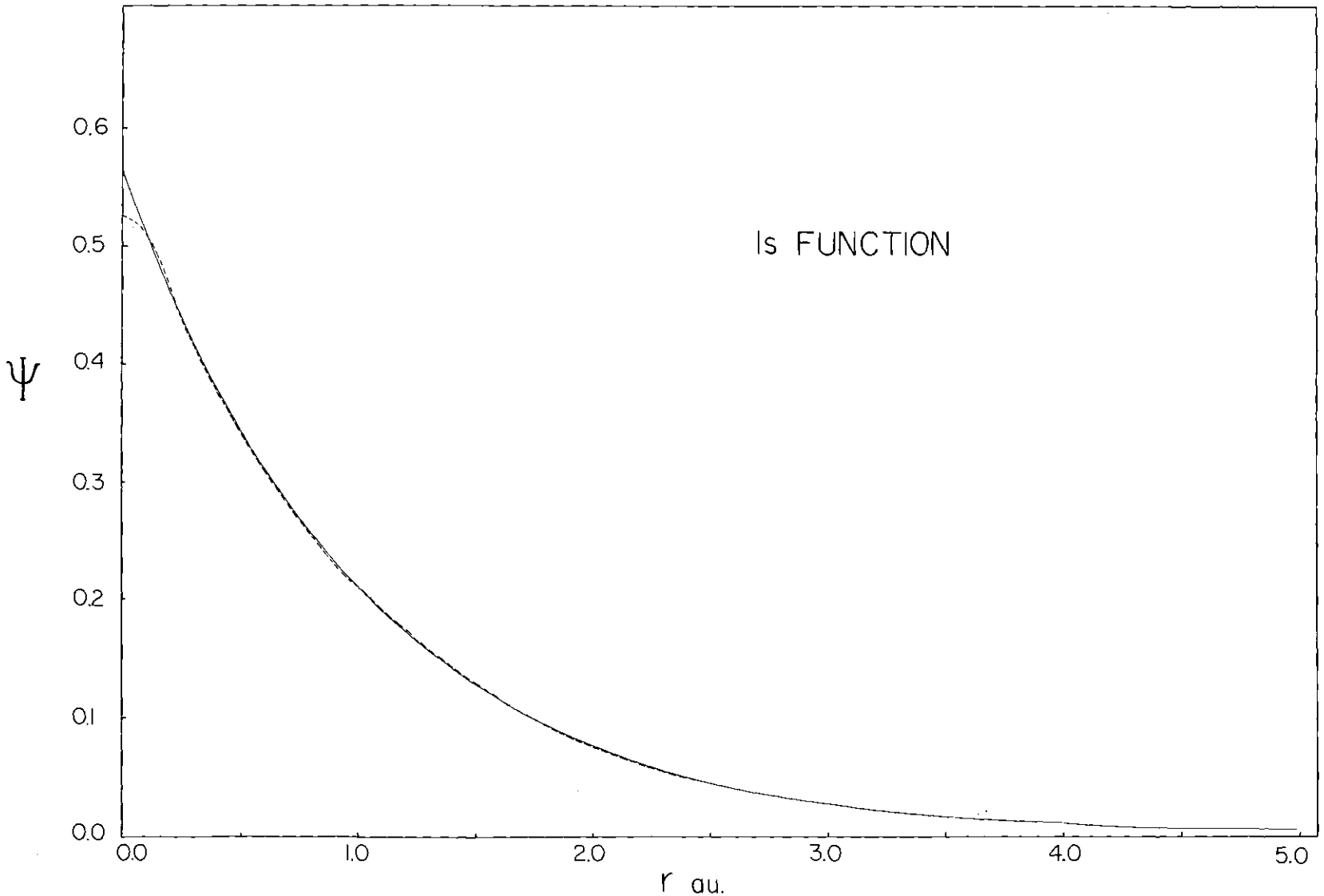

Figure 1. Radial Plot of 1s Approximation.

Table 4. Expansion of 2s Function

	Function	Energy, au.
1.	$N^{-1}\{0.899574\ \varphi_{1s} - [(2a/\pi)^{3/4}\exp(-ar^2) + 10.0(2b/\pi)^{3/4}\exp(-br^2)] + 17.3(2c/\pi)^{3/4}\exp(-cr^2)]\}$	-0.12435
	$a = 1.4$, $b = 0.034$, $c = 0.016$, $N = 23.6752$, and φ_{1s} is the unnormalized three-term approximation to the 1s function.	
2.	$N^{-1}\{1.3159\ \varphi_{1s} - [(2a/\pi)^{3/4}\exp(-ar^2) + 13.0(2b/\pi)^{3/4}\exp(-br^2) + 19.0(2c/\pi)^{3/4}\exp(-cr^2)]\}$	-0.12445
	$a = 1.4$, $b = 0.32$, $c = 0.016$, $N = 27.776$, and φ_{1s} is the unnormalized four-term approximation to the 1s function.	
3.	Exact: $(32\pi)^{-1/2}(2 - r)\exp(-r/2)$	-0.125

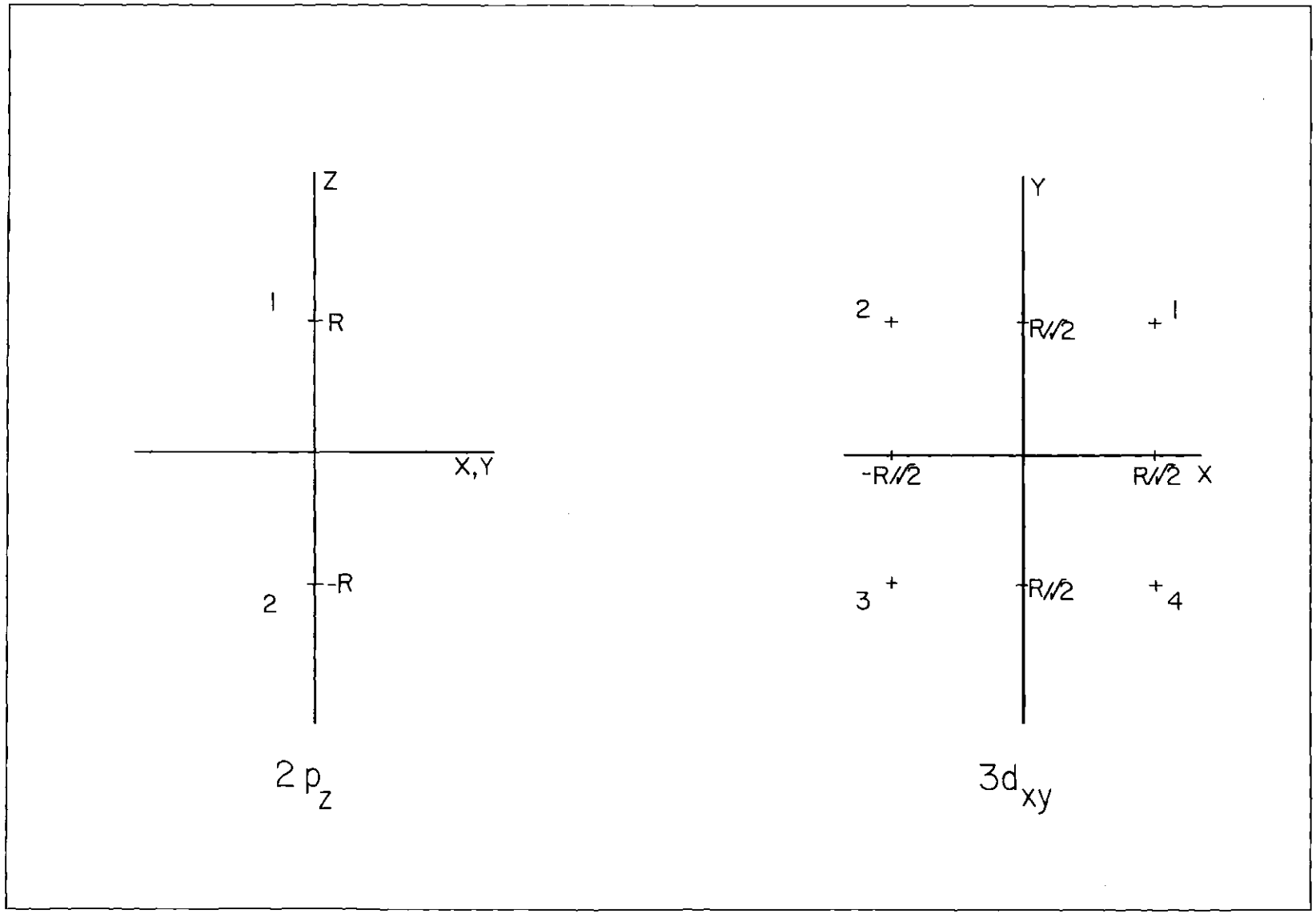

Figure 2. Origins of $2p_z$ and $3d_{xy}$ Lobe Functions.

Table 5. Expansion of 2p Function

Function, centered at R in Figure 2	Energy, au.
1. $N^{-1}(\varphi_1 - \varphi_2)$: $\varphi_k = \{(a^3/\pi)^{1/2}\ e^{-ar_k^2}\}$	-0.118590
a = 0.29, R = 1.534, N = 0.48049	
2. $N^{-1}(\varphi_1 - \varphi_2)$: $\varphi_k = \{(2a/\pi)^{3/4}\ e^{-ar_k^2}\}$	-0.113156
a = 0.045989, R = 0.93262, N = 0.39214	
3. $N^{-1}(\varphi_1 - \varphi_2)$: $\varphi_k = \{(2a/\pi)^{3/4}\ e^{-ar_k^2} + 6.1483(2b/\pi)^{3/4}\ e^{-br_k^2}\}$	-0.123081
a = 0.16875, b = 0.03375, R = 0.80, N = 2.16435	
4. $N^{-1}(\varphi_1 - \varphi_2)$: $\varphi_k = \{(2a/\pi)^{3/4}\ e^{-ar_k^2} + 9.0(2b/\pi)^{3/4}\ e^{-br_k^2} + 17.3(2c/\pi)^{3/4}\ e^{-cr_k^2}\}$	-0.124692
a = 0.305649, b = 0.0733556, c = 0.0244519, R = 0.36175, N = 3.59557	
5. Exact: $(32\pi)^{-1/2}\ r \cos\theta\ e^{-r/2}$	-0.125000

also included an approximation using exponential lobe functions. The individual Gaussian functions that make up the two-term lobe function were allowed to have different origins initially. This variation gave only a slight improvement in the energy, and thus no attempt was made to vary individual origins in the three-term lobe function. A graph of the exact $2p_z$ orbital and the three-term lobe function is given in Figure 3. The overlap of the three-term approximation with the exact $2p_z$ orbital was not calculated, but the overlap of the two-term lobe approximation with the exact function is 0.9961. Approximations for $2p_x$ and $2p_y$ are identical to the $2p_z$ approximation except for orientation along the x and y axes, respectively.

The four functions $3d_{xz}$, $3d_{yz}$, $3d_{xy}$, and $3d_{x^2-y^2}$ are identical except for orientation. No attempt was made to expand the $3d_{z^2}$ function, although an obvious choice would be to use Gaussian functions centered along the z-axis minus a linear combination centered at the origin. The $3d_{xy}$ function is expanded as the following linear combination of four lobe functions centered at points 1, 2, 3, and 4 in Figure 2. Each lobe function is composed of a linear combination of two Gaussian functions.

$$\phi_{3d_{xy}} = N^{-1}\{\phi_1 - \phi_2 + \phi_3 - \phi_4\}$$

$$\phi_k = \left\{(2a/\pi)^{3/4} e^{-ar_k^2} + 6.4\,(2b/\pi)^{3/4} e^{-br_k^2}\right\}, \quad k = 1,2,3,4$$

and

$$a = 0.035943, \quad b = 0.010783, \quad N = 0.6214, \quad R = 1.8461$$

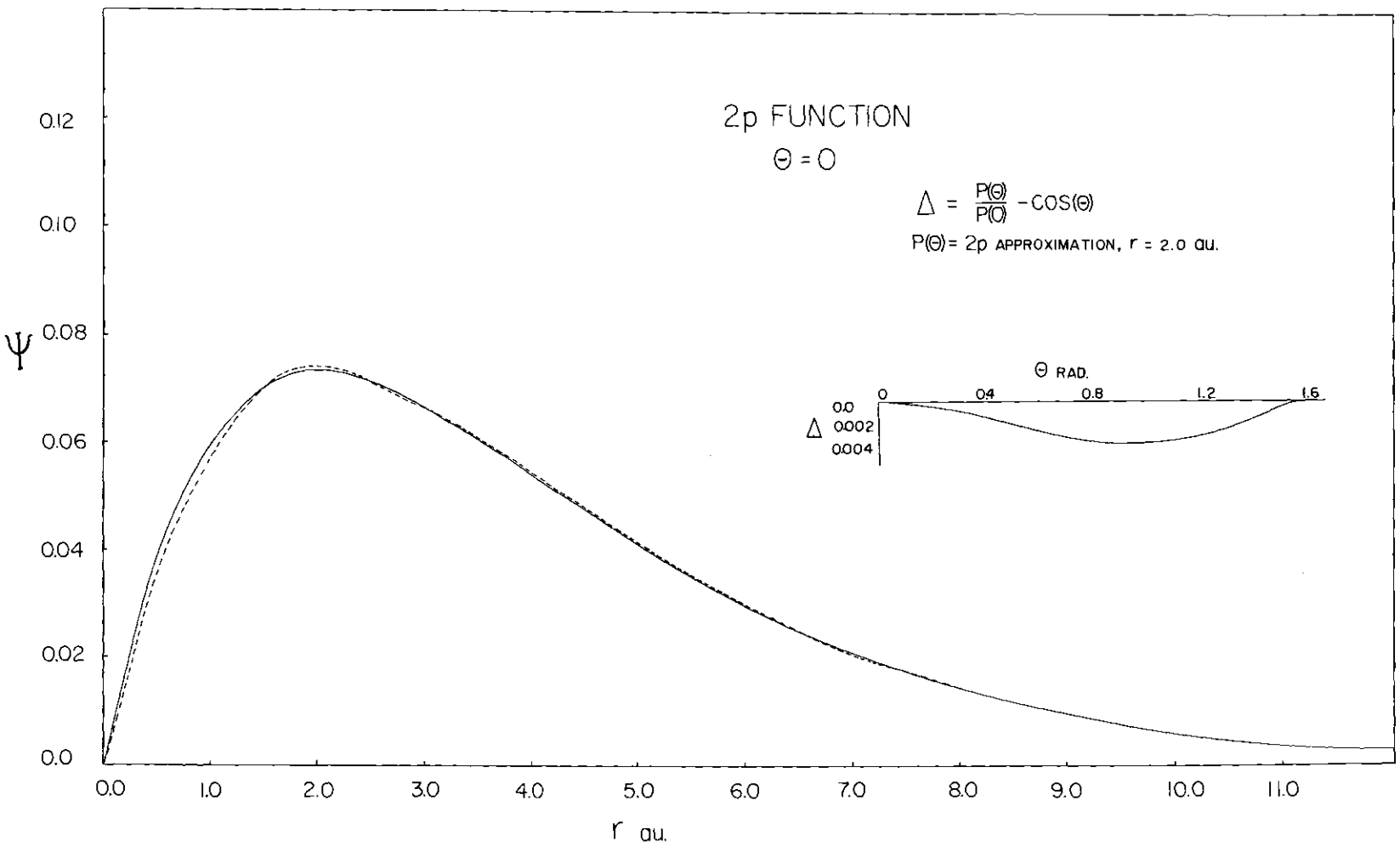

Figure 3. Graph of 2p Approximation.

The calculated energy is -0.055062 a.u. compared to the exact value of -0.0555... a.u.

It is noted that the lobe type p and d orbitals can be used to construct exact eigenfunctions of the square of the total orbital angular momentum, L^2, and also L_z, in exactly the same manner as conventional real hydrogen-like orbitals. Exactness of the eigenfunctions and eigenvalues is a consequence of the fact that the angular momentum operations depend only on rotational properties of the orbitals. That is, consider the operator, $L_z = xp_y - yp_x = -i\frac{\partial}{\partial\phi}$, in units of $\hbar$. Operation on $2p_z$ clearly gives zero; however, operation on $2p_x$ or $2p_y$ rotates one into the other with multiplication by $\pm i$.

Summary

The best approximations obtained for hydrogen-like orbitals with an effective nuclear charge Z are summarized below.

1s: $$N^{-1}\{(2a/\pi)^{3/4}\, e^{-ar^2} + 4.90(2b/\pi)^{3/4}\, e^{-br^2} + 6.70(2c/\pi)^{3/4}\, e^{-cr^2} + 0.156(2d/\pi)^{3/4}\, e^{-dr^2}\}$$

$a = 2.83994\, Z^2$, $b = 0.578897\, Z^2$, $c = 0.139452\, Z^2$, $d = 17.499\, Z^2$, $N = 11.26155$

2s: $$N^{-1}\{[2a/\pi)^{3/4}\, e^{-ar^2} + 13.0(2b/\pi)^{3/4}\, e^{-br^2} + 19.0(2c/\pi)^{3/4}\, e^{-cr^2}] - 1.31590\, \varphi_{1s}\}$$

$a = 1.4\, Z^2$, $b = 0.032\, Z^2$, $c = 0.016\, Z^2$, $N = 27.7760$, $\varphi_{1s} = 1s$ (unnormalized)

2p: $N^{-1}(\phi_1 - \phi_2)$; $\phi_k = \{(2a/\pi)^{3/4} e^{-ar_k^2} + 9.0(2b/\pi)^{3/4} e^{-br_k^2} + 17.3(2c/\pi)^{3/4} e^{-cr_k^2}\}$

$a = 0.305649\ Z^2$, $b = 0.0733556\ Z^2$, $c = 0.0244519\ Z^2$,

$N = 3.59557$, $R = 0.36175\ Z^{-1}$

$3d_{xy}$: $N^{-1}(\phi_1 - \phi_2 + \phi_3 - \phi_4)$; $\phi_k = \{(2a/\pi)^{3/4} e^{-ar_k^2} + 6.40(2b/\pi)^{3/4} e^{-br^2}\}$

$a = 0.0359425\ Z^2$, $b = 0.0107828\ Z^2$, $N = 0.62141$, $R = 1.8461\ Z^{-1}$

CHAPTER III

EVALUATION OF MOLECULAR INTEGRALS

Introduction

The philosophy expressed in this work has been to write hydrogen-like or Slater orbitals as linear combinations of Gaussian functions of the form, $\exp(-ar_k^2)$, centered at different points k in space, and thus to reduce integrals over conventional orbitals to a series of individual Gaussian function integrals. The integral of a one-electron Hermitian operator Γ, and real hydrogen-like functions χ_A and χ_B centered at points A and B in space, respectively, thus becomes

$$\langle \chi_A | \Gamma | \chi_B \rangle = \langle \sum_j c_j \phi_j | \Gamma | \sum_k c_k \phi_k \rangle$$

$$= \sum_j \sum_k c_j c_k \langle \phi_j | \Gamma | \phi_k \rangle$$

where χ_A and χ_B have been replaced by the Gaussian function expansions given in Chapter II. In case Γ is a two-electron operator, Γ_{12}, the integral

$$\langle \chi_A(1) \chi_C(2) | \Gamma_{12} | \chi_B(1) \chi_D(2) \rangle$$

reduces to,

$$\sum_j \sum_k \sum_l \sum_m c_j c_k c_l c_m \langle \phi_j(1) \phi_k(2) | \Gamma_{12} | \phi_l(1) \phi_m(2) \rangle$$

Formulas for the two basic integrals

$$\langle \phi_j | \Gamma | \phi_k \rangle$$

and

$$\langle \phi_j(1)\phi_k(2) | \Gamma_{12} | \phi_l(1)\phi_m(2) \rangle = (\phi_j(1)\phi_l(1) | \Gamma_{12} | \phi_k(2)\phi_m(2))^{\ddagger}$$

are given below for several operators Γ, and a computer program which performs the summation over individual products is included in Appendix III.

Integrals containing overlap, kinetic energy, nuclear potential, and electron repulsion operators were first derived by Boys (15), and are reproduced here for completeness. Derivations of the other integrals are given in Appendix II.

The following notation is used:

φ_A denotes a normalized Gaussian function, $(2a/\pi)^{3/4} \exp(-ar_A^2)$, with an origin at the coordinates (A_x, A_y, A_z) in space.

φ_B, φ_C, and φ_D are similarly defined relative to origins labeled B, C, and D, respectively.

$-\frac{1}{r_E}$ is a nuclear potential with origin (E_x, E_y, E_z).

AB^2 denotes the square of the distance between points A and B, $AB^2 = (A_x - B_x)^2 + (A_y - B_y)^2 + (A_z - B_z)^2$.

CD^2 denotes the square of the distance between points C and D.

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‡ The two notations which differ in the order of writing electrons 1 and 2 are introduced for convenience and are used consistently in this work.

(P_x,P_y,P_z) refers to the origin of a Gaussian function defined by the product, $\varphi_A\varphi_B$.

$$P_x = \frac{aA_x + bB_x}{a + b}, \qquad P_y = \frac{aA_y + bB_y}{a + b}, \qquad P_z = \frac{aA_z + bB_z}{a + b}$$

(Q_x,Q_y,Q_z) refers to the origin of a Gaussian function defined by the product, $\varphi_C\varphi_D$.

EP^2 denotes the square of the distance between points P and E.

$$EP^2 = (E_x - P_x)^2 + (E_y - P_y)^2 + (E_z - P_z)^2 .$$

$$F(z) = z^{-1/2} \int_0^{\sqrt{z}} \exp(-u^2)\, du, \qquad \lim_{z \to 0} F(z) = 1 .$$

Overlap

$$\langle \varphi_A | \varphi_B \rangle = \left(\frac{2}{a+b}\right)^{3/2} (ab)^{3/4} \exp\left(- AB^2 \frac{ab}{a+b} \right)$$

Kinetic Energy

$$\langle \varphi_A | -\tfrac{1}{2} \nabla^2 | \varphi_B \rangle = \langle \varphi_A | \varphi_B \rangle \left\{ \frac{3ab}{a+b} - \frac{2a^2b^2}{(a+b)^2} AB^2 \right\}$$

Nuclear Potential

$$\langle \varphi_A | -\frac{1}{r_E} | \varphi_B \rangle = -2\pi^{-\frac{1}{2}} (a+b)^{\frac{1}{2}} \langle \varphi_A | \varphi_B \rangle F(z)$$

$$z = (a+b)\, EP^2$$

Electron Repulsion

$$(\phi_A(1)\phi_B(1) \mid \frac{1}{r_{12}} \mid \phi_C(2)\phi_D(2)) = \left\{ \left[\frac{16\,(abcd)^{3/4}\,\pi^{-1/2}}{(a+b)(c+d)\,(a+b+c+d)^{1/2}} \right] \cdot \right.$$

$$\left. \exp\left(\frac{-ab}{a+b} AB^2 - \frac{cd}{c+d} CD^2 \right) F(z) \right\}$$

$$z = (a+b)(c+d)\,(a+b+c+d)^{-1}\,PQ^2$$

Quadrupole Moment

$$\langle \phi_A \mid 3z^2 - r^2 \mid \phi_B \rangle = \langle \phi_A \mid \phi_B \rangle \left\{ 2P_z^2 - P_x^2 - P_y^2 \right\}$$

where the origins of φ_A and φ_B are calculated relative to the fixed origin of the quadrupole moment operator, $3z^2 - r^2$.

Orbital Angular Momentum

$$\langle \phi_A \mid r \times p \mid \phi_B \rangle = \langle \phi_A \mid \underline{i}\, L_x + \underline{j}\, L_y + \underline{k}\, L_z \mid \phi_B \rangle$$

$$\langle \phi_A \mid L_x \mid \phi_B \rangle = \frac{2ab\sqrt{-1}}{a+b} \left\{ A_y B_z - A_z B_y \right\} \langle \phi_A \mid \phi_B \rangle$$

$$\langle \phi_A \mid L_y \mid \phi_B \rangle = \frac{2ab\sqrt{-1}}{a+b} \left\{ A_z B_x - A_x B_z \right\} \langle \phi_A \mid \phi_B \rangle$$

$$\langle \phi_A \mid L_z \mid \phi_B \rangle = \frac{2ab\sqrt{-1}}{a+b} \left\{ A_x B_y - A_y B_x \right\} \langle \phi_A \mid \phi_B \rangle$$

Spin-Spin Interaction

$$\left(\phi_A(1)\phi_B(1) \left| \frac{3z_{12}^2 - r_{12}^2}{r_{12}^5} \right| \phi_C(2)\phi_D(2)\right) = \left(\phi_A(1)\phi_B(1) \left| \frac{1}{r_{12}} \right| \phi_C(2)\phi_D(2)\right) \cdot \frac{1}{F} \cdot$$

$$\left\{ \frac{2(a+b)(c+d)}{(a+b+c+d)} \right\} \left\{ \frac{\partial F}{\partial z} + \left[\frac{2(a+b)(c+d)(P_z - Q_z)^2}{a+b+c+d} \right] \frac{\partial^2 F}{\partial z^2} \right\} + \delta$$

where

$$F = z^{-1/2} \int_0^{\sqrt{z}} e^{-u^2} du \quad , \quad z = \frac{(a+b)(c+d)\,PQ^2}{a+b+c+d}$$

and

$$\frac{\partial F}{\partial z} = \frac{1}{2} z^{-1} \left(\exp(-z) - F \right) \quad , \quad \frac{\partial^2 F}{\partial z^2} = -\frac{1}{2} z^{-1} \left(\exp(-z) + 3 \frac{\partial F}{\partial z} \right)$$

The quantity δ need not be considered in the evaluation of

$\left\langle \psi(1,2) \left| \frac{3z_{12}^2 - r_{12}^2}{r_{12}^5} \right| \psi(1,2) \right\rangle$ in case $\psi(1,2) = 0$ when electrons 1 and 2 have the same coordinates, $\vec{r}_1 = \vec{r}_2$, e.g., for a triplet state wavefunction, $\psi(1,2) = 2^{-1}\{\psi_A(1)\,\psi_B(2) - \psi_A(2)\,\psi_B(1)\}(\alpha(1)\,\beta(2) + \alpha(2)\,\beta(1))$. In general, the δ terms will not cancel otherwise.

Spin-Orbit Interaction

Evaluation of the spatial part of the spin-orbit interaction integral, $\langle \phi_A \mid S \cdot (\nabla V \times p) \mid \phi_B \rangle$, where S is the spin operator, (S_x, S_y, S_z) and V and p are the potential and momentum operators, respectively, gives

$$S_x h_x + S_y h_y + S_z h_z$$

where

$$h_x = \int \frac{Z_E}{r_E} \left(\frac{\partial \phi_A}{\partial z} \frac{\partial \phi_B}{\partial y} - \frac{\partial \phi_A}{\partial y} \frac{\partial \phi_B}{\partial z} \right) dv$$

$$h_y = \int \frac{Z_E}{r_E} \left(\frac{\partial \phi_A}{\partial x} \frac{\partial \phi_B}{\partial z} - \frac{\partial \phi_A}{\partial z} \frac{\partial \phi_B}{\partial x} \right) dv$$

$$h_z = \int \frac{Z_E}{r_E} \left(\frac{\partial \phi_A}{\partial y} \frac{\partial \phi_B}{\partial x} - \frac{\partial \phi_A}{\partial x} \frac{\partial \phi_B}{\partial y} \right) dv$$

providing V is expressed in terms of an effective potential, $+Z_E / r_E$.

Final formulas derived in Appendix II are

$$h_x = 4ab \left\{ (A_y - B_y) E_z + (B_z - A_z) E_y + B_y A_z - B_z A_y \right\} M_N Z_E$$

$$h_y = 4ab \left\{ (A_z - B_z) E_x + (B_x - A_x) E_z + B_z A_x - B_x A_z \right\} M_N Z_E$$

$$h_z = 4ab \left\{ (A_x - B_x) E_y + (B_y - A_y) E_x + B_x A_y - B_y A_x \right\} M_N Z_E$$

where,

$$M_N = -\frac{1}{EP^2} \left\{ \frac{G_N}{2(a+b)} + \pi^{-\frac{1}{2}} (a+b)^{-\frac{1}{2}} e^{-(a+b)EP^2} \langle \phi_A | \phi_B \rangle \right\}$$

$$G_N = \langle \phi_A | -\frac{1}{r_E} | \phi_B \rangle$$

If $EP^2 = 0$, M_N should be replaced by $\lim_{EP^2 \to 0} M_N$.

CHAPTER IV

APPLICATIONS OF GAUSSIAN FUNCTIONS IN ELECTRONIC ENERGY CALCULATIONS

Introduction

The results of several electronic energy calculations which were performed using the Gaussian expansions of hydrogen-like orbitals given in Chapter II are reported in this section. Primarily, the interest in these calculations was in tractibility of Gaussian function formulations and agreement with results obtained using conventional orbitals, and thus applications were restricted to relatively simple treatments, as opposed to self-consistent-field or configuration interaction methods.

Helium Atom

The energy of the helium atom was calculated using the simple product wavefunction,

$$\psi_{(1,2)} = S_A(1)\, S_A(2) \left[\frac{\alpha(1)\beta(2) - \alpha(2)\beta(1)}{\sqrt{2}} \right]$$

where α and β are spin functions and s_A represents the four-term Gaussian expansion of $\pi^{-1/2}\, a^{3/2} \exp(-ar)$. Minimization of the total energy by variation of a, or alternatively, using the scaling technique, gives

$$E = -T = -2.8393 \text{ a.u.} \quad (-77.25 \text{ ev.})$$

$$a = 1.6867$$

which compares favorably with the result obtained using an exact 1s function,

$$E = -T = 2.8477 \text{ a.u.} = -77.47 \text{ ev.}$$

$$a = 1.688$$

The experimental energy is -78.99 ev. (33).

An improved wavefunction, which has the effect of correlating electrons at different radial coordinates, is the Hylleraas function (31),

$$\psi(1,2) = \frac{S_A(1)S_B(2) + S_B(1)S_A(2)}{N}\left[\frac{\alpha(1)\beta(2) - \alpha(2)\beta(1)}{\sqrt{2}}\right]$$

where $s_A = \exp(-ar)$ and $s_B = \exp(-br)$. Energy minimization with respect to a and b gives

$$E \text{ (exact 1s)} = -T = -2.8752 \text{ a.u.} = -78.23 \text{ ev.}$$

$$a = 2.18, \qquad b = 1.19$$

$$E(\text{4-term 1s}) = -T = -2.8730 \text{ a.u.} = -78.17 \text{ ev.}$$

$$a = 2.181, \qquad b = 1.1886$$

Hydrogen Molecule Ion

The following three-center wavefunction was introduced in Chapter I.

$$\psi = N^{-1}\{S_A + \gamma S_B + S_C\}$$

where

$S_A = \exp(-ar_A)$, $S_C = \exp(-ar_C)$, $S_B = \exp(-br_B^2)$; r_A, r_C, r_B are radial coordinates from nuclei A and C, and the point midway between the nuclei, B. Minimization of the energy with respect to all

parameters including the internuclear distance gives for exact 1s functions,

$$E = -T = -0.60157 \text{ a.u.}$$

$$D^e = 2.763 \text{ ev.}$$

$$a = 1.2539, \quad b = 0.51889, \quad \gamma = 0.275$$

$$R_{AC} = 2.006 \text{ a.u.}$$

and replacing s_A and s_C by the four-term Gaussian 1s expansion gives

$$E = -T = -0.60098 \text{ a.u.}$$

$$D^e = 2.747 \text{ ev.}$$

$$a = 1.2587, \quad b = 0.52673, \quad \gamma = 0.269$$

$$R_{AC} = 2.004$$

In the latter case the dissociation energy was calculated on the basis of the exact hydrogen atom energy -0.5 a.u. If the hydrogen atom energy corresponding to the four-term 1s approximation is used,

$$D^e = (+0.60098 - 0.4990) \text{ a.u.} = 2.774 \text{ ev.}$$

Hydrogen Molecule

The following two configuration wavefunction employing a three-center molecular orbital was constructed for the hydrogen molecule.

$$\psi = \{\psi_G(1)\psi_G(2) + \lambda \psi_E(1)\psi_E(2)\}\{1+\lambda^2\}^{-\frac{1}{2}}$$

where

$$\psi_G = N^{-1}(S_A + \gamma S_B + S_C), \qquad \psi_E = N^{-1}(S_A - S_C)$$

and s_A and s_C are four-term Gaussian 1s approximations to exp(-ar), and s_B is a simple Gaussian function, $s_B = \exp(-br_B^2)$. Energy minimization with respect to all parameters gives

$$E = -T = -1.1477 \text{ a.u.}$$

$$D^e = 4.025 \text{ ev.}$$

$$a = 1.166, \quad b = 1.360$$

$$\gamma = 0.076, \quad \lambda = -0.1390$$

$$R_{AC} = 1.44 \text{ a.u.}$$

The calculated dissociation energy is approximately equal to the value obtained in Chapter I using an exponential center function. A corresponding treatment using exact 1s functions and a Gaussian center function was not performed because of the difficulty in evaluating mixed Gaussian and exponential electron repulsion integrals.

Nitrogen Atom

A seven electron wavefunction for the ^4S state of the nitrogen atom was constructed as the Slater determinant,

$$\Psi(1,2,\cdots 7) = \frac{1}{\sqrt{7!}} \det\left\{ s(1)\alpha(1)\, s(2)\beta(2)\, t(3)\alpha(3)\, t(4)\beta(4)\, x(5)\alpha(5)\, y(6)\alpha(6)\, z(7)\alpha(7) \right\}$$

where

$$s = \pi^{-\frac{1}{2}} a^{\frac{3}{2}} \exp(-ar)$$

$$t = (32\pi)^{-\frac{1}{2}} b^{\frac{3}{2}} (2 - br) \exp(-\tfrac{1}{2} br)$$

$$\begin{Bmatrix} x \\ y \\ z \end{Bmatrix} = (32\pi)^{-\frac{1}{2}} c^{\frac{5}{2}} \begin{Bmatrix} x \\ y \\ z \end{Bmatrix} \exp(-\tfrac{1}{2} cr)$$

The wavefunction as written is not an eigenfunction of the angular momentum operators L^2 and L_z, but may be reduced to a proper eigenfunction by a unitary transformation of the basis set which leaves the calculated energy invariant.

Calculations were performed by replacing the hydrogen-like orbitals by Gaussian function expansions. However, the work was done prior to the availability of the best expansions, and thus the following approximations were used.

1s: Three-term Gaussian expansion with scale factor a.

2s: Three-term Gaussian 2s expansion with scale factor b. orthogonalized to the 1s expansion with scale factor a.

2p: Two-term lobe function expansion with scale factor c.

where the explicit formulas are given in Chapter II.

The nitrogen atom energy integral, in atomic units,

$$\langle \psi(1,2,\cdots 7) \left| \left\{ \sum_{k=1}^{7} -\tfrac{1}{2}\nabla_k^2 - \frac{7}{r_k} \right\} + \sum_{i<j}^{7} \frac{1}{r_{ij}} \right| \psi(1,2,\cdots 7) \rangle$$

was minimized by variation of all exponents a, b, and c. Since orthogonal atomic orbitals are used, the expansion of the energy integral is particularly simple and has the form (32),

$$\sum_k H_{kk} + \sum_{k<l} J_{kl} - \sum_{k<l} K_{kl}$$

where the sums are over all atomic orbitals and

$$H_{kk} = \langle \phi_k | -\tfrac{1}{2}\nabla^2 - \tfrac{7}{r} | \phi_k \rangle$$

$$J_{kl} = \langle \phi_k(1)\phi_l(2) | \tfrac{1}{r_{12}} | \phi_k(1)\phi_l(2) \rangle$$

$$K_{kl} = \langle \phi_k(1)\phi_l(2) | \tfrac{1}{r_{12}} | \phi_l(1)\phi_k(2) \rangle$$

and φ_k, φ_l are atomic orbitals including spin functions; thus,

$$\phi_1 = s\alpha\,,\ \phi_2 = s\beta\,,\ \phi_3 = t\alpha\,,\ \phi_4 = t\beta\,,\ \text{etc.}$$

The results of the energy minimization are:

$E = -T = -53.81674$ a.u.

a = 6.6964

b = 4.5077

c = 3.7063

E(experimental (33)) = -54.611 a.u.

Much of the 0.79 a.u. discrepancy between the calculated and experimental value is due to the following Gaussian expansion error.

1s:	$2(0.5 - 0.4970)a^2$	= 0.277 a.u.
2s:	$2(0.125 - 0.1245)b^2$	= 0.028 a.u.
2p:	$3(0.125 - 0.1231)c^2$	= 0.083 a.u.
	Total	0.388 a.u.

where the error terms are computed on the basis of one electron energy differences between exact and approximate hydrogen-like orbitals. The

use of the more accurate expansions given in Chapter II should bring the calculated energy into fairly close agreement with a value of -54.2652 obtained using exact Slater orbitals (23). It is of interest to note that the energy calculated above is considerably better than a recently reported value of -53.1769 a.u. obtained using a conventional Gaussian function formulation (23).

Nitrogen Molecule

A calculation of the energy of the ground electronic state of the nitrogen molecule was performed using a simple molecular orbital formulation, but by explicitly taking into account all electron repulsion interactions of the fourteen electrons. The problem thus is quantum mechanically one of considerable magnitude and as such it provides a test of the tractibility of the Gaussian function formulation.

The wavefunction was constructed as the determinant of molecular orbitals,

$$\Psi(1,2,\cdots,14) = \frac{1}{\sqrt{14!}} \det\{S_1\alpha(1)\,S_1\beta(2)\,S_2\alpha(3)\,S_2\beta(4)\,T_1\alpha(5)\,T_1\beta(6)\,T_2\alpha(7)\,T_2\beta(8) \cdot X\alpha(9)\,X\beta(10)\,Y\alpha(11)\,Y\beta(12)\,Z\alpha(13)\,Z\beta(14)\}$$

where the molecular orbitals are the simple (orthogonalized) bonding and antibonding ones obtained for each pair of atomic orbitals on separate nuclei A and B. Thus

$$S_1 = N^{-1}\{s_A + s_B\}$$

$$S_2 = N^{-1}\{s_A - s_B\}$$

$$T_1 = N^{-1}\{(t_A + t_B) - dS_1\}$$

$$T_2 = N^{-1}\{(t_A - t_B) - eS_2\}$$

$$X = N^{-1}\{x_A + x_B\}$$

$$Y = N^{-1}\{y_A + y_B\}$$

$$Z = N^{-1}\{(z_A + z_B) - fT_1 - gS_1\}$$

and s, t, x, y, and z are, respectively, the 1s, 2s, and 2p Gaussian atomic orbitals (unnormalized) used in the N atom calculation. Atomic orbital normalizations were included in the molecular orbital normalization constants and constants d, e, f, and g were chosen to make the set of molecular orbitals mutually orthogonal.

The nitrogen molecule energy integral,

$$\left\langle \psi(1,2,\cdots 14) \left| \left\{ \sum_{k=1}^{14} -\tfrac{1}{2}\nabla_k^2 - \frac{7}{r_{Ak}} - \frac{7}{r_{Bk}} \right\} + \sum_{i<j}^{14} \frac{1}{r_{ij}} + \frac{49}{R_{AB}} \right| \psi(1,2,\cdots 14) \right\rangle$$

was evaluated at the experimental internuclear distance $R_{AB} = 2.06916$ a.u. Since the molecular orbitals are orthogonal, the integral may be expanded just as in the N atom; however, the matrix elements, H_{kk}, $J_{k\ell}$, and $K_{k\ell}$, previously defined now refer to integrals over molecular orbitals. The one electron integrals and normalization and orthogonalization constants are given in Table 6 and electron repulsion integrals are included in Appendix VI.

One electron "molecular orbital energies, E_{mo}," are also given in the table where E_{mo} is defined as the decrease in energy which

Table 6. Nitrogen Molecule Molecular Orbital Energies and One-Electron Integrals

	Normalization Constants	Kinetic Energy (a.u.)	Nuclear Attraction Energy (a.u.)	E_{mo} (a.u.)
S_1	19.77891	22.285937	-49.975135	-25.11153
S_2	19.77890	22.285983	-49.975156	-25.11153
T_1	43.023515	1.955271	-10.895968	-5.74933
T_2	27.446691	2.587038	-10.534159	-3.97667
Z	3.358911	1.777471	-9.963802	-3.09860
X,Y	3.487767	1.456063	-9.9331243	-1.33521

d = 1.70538 e = -1.70538 f = 1.158081 g = 0.287771

results upon population of all degenerate molecular orbital divided by the total number of electrons in the degenerate orbitals.

Energy results are:

Nuclear attraction energy	-300.01342 a.u.
Kinetic energy	107.60765
Electron repulsion energy	60.96962
Nuclear repulsion energy	23.68110
Total energy	-107.75505
Energy of separated atoms	-107.63347
Dissociation energy	0.1216 a.u. = 3.31 ev.
Experimental dissociation energy (41,42)	9.76 ev.

An approximate ionization potential of 0.5321 a.u. (14.49 ev.) was determined by removing one electron from the π system and recalculating the total energy using the same molecular orbital parameters.

Conclusion

The results of the electronic energy calculations are clearly significant. In the helium atom, hydrogen molecule, and hydrogen molecule ion applications, the energies calculated using Gaussian function expansions are in close agreement with the conventional orbital results, but in the nitrogen atom application in which the best expansions were not used, there is a significant error in the calculated total energy. This error can be attributed in part to inadequacies in the hydrogen-like orbital approximations which become magnified at large effective nuclear

charges, and as such can be largely eliminated by using the more accurate Gaussian expansions.

Primarily, the nitrogen molecule calculation is a demonstration of the tractibility of the Gaussian function formulation, and does not constitute a successful calculation of the dissociation energy. This is, of course, a consequence of the simple molecular orbital formulation, and is not due to the Gaussian function approximation. The fact that no difficulties were encountered in the evaluation of multicenter electron repulsion integrals is a demonstration of the utility of the Gaussian function formulation.

CHAPTER V

PROPOSED APPLICATIONS OF GAUSSIAN FUNCTIONS

The use of Gaussian functions in the representation of electronic wavefunctions is receiving increased attention, and although problems still exist, it is not unreasonable to expect extensive application to conventional self-consistent-field calculations of molecules. All methods currently employed involve an expansion of the radial parts of the wavefunctions only; the angular parts are retained as spherical harmonics. In this thesis explicit dependence on the angular variables θ and φ is eliminated, and conventional orbitals are expanded as linear combinations of Gaussian functions with origins judiciously located at different points in space.

There are considerable difficulties associated with the conventional technique using angular variables since integral formulas for these functions must be generated from more basic formulas of simple Gaussian functions. This problem is not exceptionally difficult mathematically, but practically, elaborate computational schemes are required in all but the simplest molecules. The anticipated complexity of the practical problem thus is not encouraging, and in particular, d-orbital treatments in any system except atoms seem prohibitively difficult. Of still greater complexity than conventional energy calculations is the evaluation of higher order interaction energies such as those which are due to spin-spin and

spin-orbit interactions. Again, calculations are practicable for simple systems or for very approximate one-term Gaussian orbitals.

In the nonangular formulation of this thesis only one set of particularly simple integral formulas is required. Therefore the approach should be useful in conventional molecular energy calculations requiring the evaluation of electron repulsion integrals, and should be of even greater utility in the evaluation of various interaction energies, quadrupole and magnetic moments, etc. Examples of the latter applications are found in Part II of the thesis which concerns the triplet state of glyoxal and magnetic interactions.

In a more novel application, the p-orbital of this work can be used in a formulation analogous to Dewar's split-p-orbital method (26, 27). Briefly, the method involves an artificial separation of the conventional p-orbital, e.g., $(32\pi)^{-1/2}\ r \cos\theta \exp(-r/2)$, into two lobes, and a subsequent correlation of electrons with opposite spins into the separate lobe regions. Applications have been quite successful, but they are by no means rigorous since interactions with sigma electrons have been ignored. Certain justifications for neglecting this interaction can be found if conventional p-orbitals are used, but not if the lobes are separated, since orthogonality properties then are destroyed. It is not easy to orthogonalize individual lobes with inner shell orbitals in the case of conventional p-orbitals, but the orthogonalization is easily performed using the p-orbital of this work which already is constructed as the difference of two lobe functions. The lobe functions, however,

are not at all equivalent to Dewar's lobe functions, but the basic method of correlation is retained.

Another application that is of more theoretical interest concerns the correlation of electrons in molecular orbitals. The desirability of correlating pairs of electrons is well known (28), but a tractable mathematical formulation is lacking. It is possible, however, to formulate the problem in terms of Gaussian orbital expansions, and to introduce explicitly the interelectronic distance, r_{12}, into the molecular orbital function. This method is based on Hylleraas' very successful treatment of the helium atom in which the two electron function

$$\psi(1,2) = N^{-1}(1 + cr_{12})\psi(1)\psi(2)$$

was used, where ψ is a scaled hydrogen-like 1s orbital and c is a variational parameter. A total energy of -78.63 ev. compared with the experimental value of -78.99 ev. was obtained.

A corresponding treatment of the hydrogen molecule was performed by Frost and Braunstein (30) without much improvement in the dissociation energy over the value obtained by simple treatments. However, the failure of this treatment likely is due to a poor one electron function, since only a simple 1s molecular orbital was used, and not necessarily to inadequate electron correlation.

The above correlation method is applicable to any molecular orbital; however, although the idea is attractive, its success has certainly not been demonstrated.

PART II

MAGNETIC INTERACTIONS IN THE TRIPLET STATE OF GLYOXAL

CHAPTER VI

THE TRIPLET STATE OF GLYOXAL AND OBJECTIVES OF THE THEORY

The spectrum of gaseous glyoxal, $(CHO)_2$, in the region around 5000 Å which is ascribed by Brand (34) to a singlet-triplet transition has been studied by Eberhardt *et al.* (35). Assignment as a singlet-triplet transition is suggested by the occurrence of a well-known singlet-singlet transition which has origin at 4550 Å (34,36), and which likely corresponds to a promotion of one of the nonbonding oxygen electrons to the lowest unfilled molecular orbital. The triplet state is then described approximately in terms of the same molecular orbital configuration as the excited singlet state, but with unpaired electron spins. Electrons in the unpaired spin state are automatically correlated by the Pauli antisymmetry principle to give a lower electron repulsion energy and hence a lower total energy for the electronic state.

The geometry of the excited state is tacitly assumed to be the same as the generally accepted trans coplanar geometry of the ground state, although nonplanar geometries are certainly imaginable.

Relatively weak absorption found in the 5000 Å region as compared with the singlet-singlet region is consistent with the singlet-triplet assignment since such transitions are initially forbidden, but become allowed by spin-orbit mixing with singlet states. There is also

the possibility of a singlet-singlet transition in the same region caused by a magnetic dipole absorption of radiation, or perhaps a vibronic mechanism; thus, the 5000 Å region is likely a superposition of both the singlet-triplet and singlet-singlet transitions.

One of the objectives of this work is to perform a theoretical calculation of probabilities for the singlet-triplet transition and the singlet-singlet magnetic dipole transition. A second objective concerns the theoretical treatment of magnetic interactions in the triplet state, and thus involves a calculation of spin-spin, spin-orbit, and spin-rotational interactions.

The main interest in the 5000 Å region, however, is due to the occurrence of a magnetic rotation spectrum (35) which according to current theory is related to the triplet character of a state, and consequently is not found in singlet-singlet transitions. Experimentally, samples are subjected to a relatively weak magnetic field, (2000 Gauss), and irradiated with plane polarized radiation with a direction of propagation along the axis of the field. The transmitted radiation is then observed along the axis, but only for a polarization perpendicular to the initial direction of polarization. The resulting spectrum is called a magnetic rotation spectrum, MRS, and for optically inactive molecules is typified by sets of relatively sharp lines in regions corresponding to absorption frequencies.

Since lines are relatively sharp in MRS as compared with absorption, the technique offers some hope for obtaining more detailed information about triplet states. However, in glyoxal large differences appear

in the detailed structure between MRS and absorption, and therefore a determination of the effect of the external magnetic field on the unperturbed energy levels is desirable. This is a third objective of this work.

CHAPTER VII

ELECTRONIC WAVEFUNCTIONS

General Theory

A general method of constructing electronic wavefunctions for molecules involves the expansion of molecular orbitals as linear combinations of atomic orbitals centered at each nucleus assuming the Born-Oppenheimer approximation of nuclei clamped in an equilibrium configuration. Thus,

$$\psi_j = \sum_k c_k \phi_k$$

where ϕ_k is an atomic orbital. Atomic orbital parameters are variable in principle, but usually the choice of self-consistent-field free-atom values is made. Expansion coefficients are determined in part by molecular symmetry subject to a restriction that resulting molecular orbitals be both normalized and mutually orthogonal.

Multi-electron wavefunctions are then formulated as antisymmetrized products of molecular orbitals occupied in accordance with the Pauli exclusion principle (37). The ground singlet state of a 2N-electron molecule thus is described in terms of a set of doubly occupied molecular orbitals, $\psi_1, \psi_2, \ldots, \psi_N$, used in a Slater determinant formulation of the antisymmetric wavefunction,

$$\Psi = \frac{1}{\sqrt{2N!}} \det \left\{ \psi_1(1)\alpha(1)\,\psi_1(2)\beta(2) \cdots \psi_N(2N-1)\alpha(2N-1)\,\psi_N(2N)\beta(2N) \right\}$$

in which each molecular orbital occurs twice, once with each spin function α and β.

Three component functions corresponding to 0 and ± 1 eigenvalues of the spin operator S_z are obtained for a triplet state.

$$\Psi_{+1} = \frac{1}{\sqrt{2N!}} \det\left\{ \psi_1(1)\alpha(1)\, \psi_1(2)\beta(2)\, \psi_2(3)\alpha(3) \cdots \psi_N(2N-1)\alpha(2N-1)\, \psi_{N+1}(2N)\alpha(2N) \right\}$$

$$\Psi_0 = \frac{2^{-\frac{1}{2}}}{\sqrt{2N!}} \det\left\{ \psi_1(1)\alpha(1)\, \psi_1(2)\beta(2)\, \psi_2(3)\alpha(3) \cdots \psi_N(2N-1)\alpha(2N-1)\, \psi_{N+1}(2N)\beta(2N) \right\}$$

$$+ \frac{2^{-\frac{1}{2}}}{\sqrt{2N!}} \det\left\{ \psi_1(1)\alpha(1)\, \psi_1(2)\beta(2)\, \psi_2(3)\alpha(3) \cdots \psi_N(2N-1)\beta(2N-1)\, \psi_{N+1}(2N)\alpha(2N) \right\}$$

$$\Psi_{-1} = \frac{1}{\sqrt{2N!}} \det\left\{ \psi_1(1)\alpha(1)\, \psi_1(2)\beta(2)\, \psi_2(3)\alpha(3) \cdots \psi_N(2N-1)\beta(2N-1)\, \psi_{N+1}(2N)\beta(2N) \right\}$$

The wavefunction for the singlet state corresponding to the same molecular orbital configuration as the triplet is the same as Ψ_0 except for a subtraction of the two determinants.

The ground state energy is obtained by minimizing the expectation value of the molecular Hamiltonian with respect to all variable parameters in the wavefunction. In excited states the energy is also minimized, but with the added requirement that excited state wavefunctions remain orthogonal to all lower energy eigenfunctions. Resulting wavefunctions are considered to afford the best description of electronic states within the framework of the theory. Calculations of ground state dissociation energies, however, are usually not in good agreement with

experiment. The failure is attributed to inadequate electron correlation, and as such can be corrected by including additional molecular orbital configurations. Correlation errors in triplet states are expected to be much less significant than in singlet states since the Pauli principle provides an automatic correlation of electrons with parallel spins.

The present application to glyoxal concerns primarily the lowest excited triplet state, and perturbations of this state by rotational, spin-orbit, and spin-spin interactions. Absolute energies are not calculated; instead, excited state wavefunctions are deduced mainly from general considerations plus some quantitative results available from a self-consistent-field treatment of formaldehyde (40). Since calculations are of a perturbation nature, slight errors in wavefunctions are not expected to seriously affect the conclusions.

Molecular Orbitals

The following carbon and oxygen atomic orbitals are used as a basis for molecular orbitals in glyoxal.

$$2s = Z^{\frac{3}{2}} (32\pi)^{-\frac{1}{2}} (2 - Zr) \exp(-\tfrac{1}{2} Zr)$$

$$2p = Z^{\frac{5}{2}} (32\pi)^{-\frac{1}{2}} \left\{ \begin{matrix} x \\ y \\ z \end{matrix} \right\} \exp(-\tfrac{1}{2} Zr)$$

where,

$$Z_{carbon} = 3.1062$$

$$Z_{oxygen} = 4.4456$$

Effective nuclear charges, Z, for 2p orbitals are the self-consistent field values for atoms tabulated by Roothaan (38), and are approximately equal to those predicted by Slater rules (39). Choice of the same value of Z for $2p_x$, $2p_y$, $2p_z$, and 2s orbitals is not required, but is due to a lack of more detailed information. In actual computations atomic orbitals were replaced by the Gaussian function expansions discussed in Chapter II,

$$2p = N^{-1}(\varphi_1 - \varphi_2): \varphi_k = \{(2a/\pi)^{3/4} \exp(-ar_k^2) + 9.0(2b/\pi)^{3/4} \exp(-br_k^2) + 17.3(2c/\pi)^{3/4} \exp(-cr_k^2)\}$$

where $a = 0.305679\ Z^2$, $b = 0.073355\ Z^2$, $c = 0.0244519\ Z^2$,

$$2s = N^{-1}\{0.899574\ \varphi_{1s} - [(2a/\pi)^{3/4} \exp(-ar^2) + 10.0(2b/\pi)^{3/4} \exp(-br^2) + 17.3(2c/\pi)^{3/4} \exp(-cr^2)]\}$$

where $a = 1.4\ Z^2$, $b = 0.034\ Z^2$, $c = 0.016\ Z^2$, and φ_{1s} is the unnormalized-three-term 1s approximation given in Table 3.

The location and designation of atomic and hybrid orbitals is shown in Figure 4. The solid lines lie in the molecular plane, and the dashed lines, which represent the p_π orbitals, are perpendicular to the plane. The functions indicated in the figure are defined below.

q_1, p_1^o: 2p oxygen

p_1^c : 2p carbon

s_1^s : oxygen sp hybrid, $(2s - \ell_5(2p))(1 + \ell_5^2)^{-1/2}$

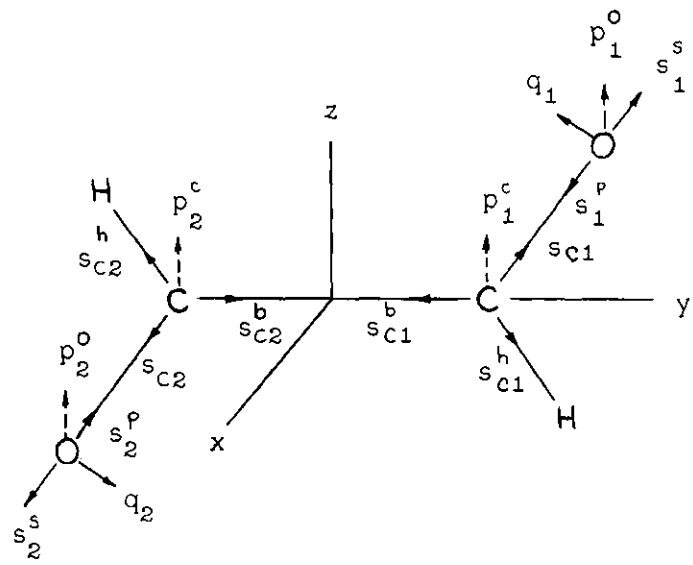

Figure 4. Glyoxal Atomic Orbitals

s_1^p : oxygen sp hybrid, $(\ell_5(2s) + 2p)(1 + \ell_5^2)^{-1/2}$

s_{c1}: carbon sp^3 hybrid, $\frac{1}{\sqrt{3}}(2s) + \frac{1}{\sqrt{6}}(2p_y) - \frac{1}{\sqrt{2}}(2p_x)$

s_{c1}^h: carbon sp^3 hybrid, $\frac{1}{\sqrt{3}}(2s + \frac{1}{\sqrt{6}}(2p_y) + \frac{1}{\sqrt{2}}(2p_x)$

s_{c1}^b: carbon sp^3 hybrid, $\frac{1}{\sqrt{3}}(2s) - \sqrt{\frac{2}{3}}\ (2p_y)$

Similar definitions apply to carbon and oxygen nuclei labeled by a 2. Molecular orbitals and their transformation properties relative to the C_{2h} point group are listed below. The C_{2h} character table (32) referred to the axes shown in Figure 4 is

	E	C_2	σ_h	i	
A_g	1	1	1	1	R_z, x^2, y^2, z^2, xy
A_u	1	1	-1	-1	z
B_g	1	-1	-1	1	R_x, R_y, xz, yz
B_u	1	-1	1	-1	x, y

$\psi_1 = N_1^{-1}(p_1^o + \ell_1 p_1^c + \ell_1 p_2^c + p_2^o)$ a_u $(\ell_1 = 1.0)$

$\psi_2 = N_2^{-1}(p_1^o + \ell_2 p_1^c - \ell_2 p_2^c - p_2^o)$ b_g $(\ell_2 = 1.0)$

$\psi_3 = N_3^{-1}(\ell_3 p_1^o - p_1^c - p_2^c + \ell_3 p_2^o)$ a_u $(\ell_3 = 1.0)$

$\psi_4 = N_4^{-1}(\ell_4 p_1^o - p_1^c + p_2^c - \ell_4 p_2^o)$ b_g $(\ell_4 = 1.0)$

$\psi_5 = N_5^{-1}(q_1 + q_2)$ a_g

$\psi_6 = N_6^{-1}(q_1 - q_2)$ b_u

$$\psi_7 = N_7^{-1}(s_1^s + s_2^s) \qquad a_g$$

$$\psi_8 = N_8^{-1}(s_1^s - s_2^s) \qquad b_u$$

$$\psi_9 = N_9^{-1}(s_{c1}^b + s_{c2}^b) \qquad a_g$$

$$\psi_{10} = N_{10}^{-1}(s_{c1}^b - s_{c2}^b) \qquad b_u$$

$$\psi_{11} = N_{11}^{-1}(\ell_{11}\, s_{c1} + s_1^p + \ell_{11}\, s_{c2} + s_2^p) \qquad a_g \qquad (\ell_{11} = 1.0)$$

$$\psi_{12} = N_{12}^{-1}(s_1^p + \ell_{12}\, s_{c1} - \ell_{12}\, s_{c2} - s_2^p) \qquad b_u \qquad (\ell_{12} = 1.0)$$

$$\psi_{13} = N_{13}^{-1}(s_1^p - \ell_{13}\, s_{c1} - \ell_{13}\, s_{c2} + s_2^p) \qquad a_g \qquad (\ell_{13} = 1.0)$$

$$\psi_{14} = N_{14}^{-1}(s_1^p - \ell_{14}\, s_{c1} + \ell_{14}\, s_{c2} - s_2^p) \qquad b_u \qquad (\ell_{14} = 1.0)$$

The molecular orbitals ψ_1, ψ_2, ψ_9, ψ_{11}, and ψ_{12} are bonding; ψ_3, ψ_4, ψ_{10}, ψ_{13}, and ψ_{14} are antibonding; ψ_5, ψ_6, ψ_7, and ψ_8 are nonbonding.

Numerical coefficients used in subsequent calculations are indicated in parenthesis. Those for the π molecular orbitals are chosen on the basis of Goodfriend, Birss, and Duncan's self-consistent-field calculation of formaldehyde (40) in which essentially no polarity in the C-O π and π^* bonds was found. The nonbonding sp hybrid on oxygen is estimated at one-third 2p character, $(\ell_5 = 1/3)$, and polarization in the carbon-oxygen sigma bond is neglected, $(\ell_{11} = \ell_{12} = \ell_{13} = \ell_{14})$. Some justification for this rather casual dismissal of sigma parameters may be found by anticipating the results of the calculations, where it

is evident that the sigma system is much less significant than the π system.

Normalization constants for the π molecular orbitals were calculated exactly, but those for the σ molecular orbitals were approximated by assuming equal overlap of carbon-oxygen sigma orbitals and carbon-carbon sigma orbitals. The resulting numerical values are:

$N_5 = \sqrt{2}$	$N_1 = 2.3406$	$N_9 = 1.65$
$N_6 = \sqrt{2}$	$N_2 = 2.0885$	$N_{10} = 1.14$
$N_7 = \sqrt{2}$	$N_3 = 1.8723$	$N_{11} = 2.33$
$N_8 = \sqrt{2}$	$N_4 = 1.629$	$N_{14} = 1.89$

Ground and Excited State Configurations

The ground state of glyoxal corresponds to a double occupation of each bonding and nonbonding molecular orbital to give the configuration,

$$\psi_9^2\ \psi_{11}^2\ \psi_{12}^2\ \psi_7^2\ \psi_8^2\ \psi_1^2\ \psi_2^2\ \psi_5^2\ \psi_6^2$$

Excited states correspond to a promotion from one of the bonding or nonbonding orbitals to an antibonding orbital; thus, the first few low energy states are

(1.) $\psi_5 \rightarrow \psi_3$ $(\pi^* \leftarrow n)$ $^{1,3}A_u$

(2.) $\psi_6 \rightarrow \psi_3$ $(\pi^* \leftarrow n)$ $^{1,3}B_g$

(3.) $\psi_5 \rightarrow \psi_4$ $(\pi^* \leftarrow n)$ $^{1,3}B_g$

(4.) $\psi_6 \rightarrow \psi_4$ $(\pi^* \leftarrow n)$ $^{1,3}A_u$

etc.

where the symmetry and singlet or triplet character of each excited state is indicated.

CHAPTER VIII

ELECTRIC AND MAGNETIC DIPOLE TRANSITION PROBABILITIES

Radiation Theory

A purely quantum mechanical treatment of the interaction of radiation with matter requires, in addition to a quantization of particle observables, a rigorous quantization of the radiation field (43). In the highly successful semiclassical theory, however, the field quantization is omitted, and instead the field is characterized only by fundamental electric and magnetic field intensities E and $\mathcal{H}$, and the Maxwell equations. Particles in motion in the field then are assumed to experience classical electric and magnetic forces. A consideration of these forces on a particle of mass m, charge e (esu), and momentum p leads to the Hamiltonian (32, 43),

$$H = \frac{1}{2m}\left[\left(P_x - \frac{e}{c} A_x\right)^2 + \left(P_y - \frac{e}{c} A_y\right)^2 + \left(P_z - \frac{e}{c} A_z\right)^2 \right] + e\varphi$$

where E and $\mathcal{H}$ have been replaced by a vector potential A, and scalar potential φ, with the definitions,

$$\mathcal{H} = \nabla \times A$$

$$E = -\frac{1}{c}\frac{\partial A}{\partial t} - \nabla\varphi$$

A complete specification of A and φ requires an additional condition, the so-called choice of gauge (45), where the Lorentz gauge corresponds to the condition,

$$\nabla \cdot A + \frac{1}{c} \frac{\partial \phi}{\partial t} = 0$$

and the Coulomb gauge to

$$\nabla \cdot A = 0$$

In addition, the scalar potential ϕ may be chosen as zero for a pure radiation field, i.e., in absence of external electric and magnetic fields (43).

Expansion of the Hamiltonian using the Coulomb gauge gives,

$$H = \frac{1}{2m} p^2 - \frac{e}{mc} A \cdot p + \frac{e^2}{c^2} |A|^2$$

for a one-particle system, and

$$H = \sum_{k}^{n} \left(\frac{1}{2m} p_k^2 - \frac{e}{mc} A \cdot p_k + \frac{e^2}{c^2} |A|^2 \right) + \sum_{i<j}^{n} V_{ij}$$

for a system of n identical particles with interaction energy V_{ij} between particles. The e and m must be replaced by individual charges and masses in case the particles are not identical, but in the present application only electrons are considered.

It may be shown by an expansion of matrix elements that the $A \cdot p$ and $|A|^2$ terms correspond to one and two quantum processes, respectively. The latter is generally negligible, but the process could correspond to a simultaneous absorption and emission. Further consideration (43) shows that matrix elements of $|A|^2$ vanish for an emitted photon polarized perpendicular to the absorbed photon, and consequently the term would not contribute to a magnetic rotation spectrum.

Thus, neglecting $|A|^2$, the entire interaction of radiation with a system of electrons is due to the term

$$H' = -\frac{e}{mc}\sum_k A\cdot p_k$$

In the usual theory of absorption of radiation by electrons in a molecule (32), H' is treated as a time dependent perturbation of the molecular Hamiltonian, H_o, and the effect of the interaction is expressed as a mixing of initially well defined molecular states. If the solutions of the time dependent Schrödinger equation,

$$H_o\Psi = i\hbar\frac{\partial\Psi}{\partial t}$$

are

$$\psi_o^\circ e^{-iE_ot/\hbar} \qquad \psi_1^\circ e^{-iE_1t/\hbar} \qquad \cdots \qquad \psi_n^\circ e^{-iE_nt/\hbar}$$

then in the presence of the radiation field the wavefunction is expanded as

$$\Psi(t) = c_o(t)\,\psi_o^\circ e^{-iE_ot/\hbar} + \cdots + c_n(t)\,\psi_n^\circ e^{-iE_nt/\hbar}$$

Assuming that the molecule is in a certain state, say the lowest state ψ_o, at time $t = 0$, then at a later time t, the square of the magnitude of $c_n(t)$ represents the probability that a transition to state n has occurred. The details of the well-known treatment are not considered here, but are given for example by Eyring, Walter, and Kimball of Heitler (32, 43). The results show a dependence of

$c_n(t)$ on the interaction matrix element

$$\left\langle \psi_o^\circ e^{-iE_o t/\hbar} \left| -\frac{e}{mc} \sum_k A \cdot p_k \right| \psi_n^\circ e^{-iE_n t/\hbar} \right\rangle$$

In order to proceed further, it is necessary to define the vector potential, A, relative to a molecular coordinate system with origin at the center of mass. Expansion of A over the dimensions of the molecule gives the result for one particle (32, 44)

$$A \cdot p = A_x^\circ p_x + A_y^\circ p_y + A_z^\circ p_z$$
$$- \frac{i\hbar}{2} \mathcal{H}_x^\circ \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) - \frac{i\hbar}{2} \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) - \frac{i\hbar}{2} \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$$

+ quadrupole and higher order terms

where superscript zeros imply evaluation of A and $\mathcal{H}$ at the center of mass of the molecule.

The expansion thus permits a separation of the A·p matrix element into a time dependent part which contains the radiation field quantities A° and $\mathcal{H}^\circ$, and the exponential energy functions, and a time independent part that depends on the stationary state wavefunctions ψ_m° and ψ_n°.

Since the previous derivation is nonrelativistic, electron spin must be introduced as an assumption. Spin angular momenta appear added to each orbital angular momentum term to give

$$A \cdot p = A_x^\circ p_x + A_y^\circ p_y + A_z^\circ p_z +$$

$$+ \tfrac{1}{2}\mathcal{H}_x^\circ (M_x + 2S_x) + \tfrac{1}{2}\mathcal{H}_y^\circ (M_y + 2S_y)$$

$$+ \tfrac{1}{2}\mathcal{H}_z^\circ (M_z + 2S_z) + \cdots$$

where the orbital angular momentum operators,

$$M_x = -i\hbar \left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y} \right) \text{ etc.}$$

have been introduced and a spin g-factor equal to two has been assumed.

Transition Probability

The results of the previous section give the following explicit expression for the probability of a transition in unit time from the state ψ_o to the state ψ_n corresponding to an absorption of radiation (32).

$$B_{n\leftarrow o}\rho(\nu) = \frac{2\pi}{3\hbar^2}\Big\{ \Big| \langle \psi_o | e \sum_k \underline{i} x_k + \underline{j} y_k + \underline{k} z_k | \psi_n \rangle \Big|^2$$

$$+ \Big\langle \psi_o \Big| \frac{e}{2mc} \sum_k \underline{i}\,(M_x + 2S_x)_k + \underline{j}\,(M_y + 2S_y)_k + \underline{k}\,(M_z + 2S_z) \Big| \psi_n \Big\rangle \Big|^2$$

$$+ \text{quadrupole and higher terms} \Big\} \rho(\nu)$$

where the sums are over all electrons, $B_{n\leftarrow o}$ is the Einstein transition probability coefficient for absorption, and $\rho(\nu)$ is the energy density of the radiation field which is equal to the average values of the squared electric and magnetic field strengths,

$$\rho(\nu) = \frac{1}{4\pi}\overline{E^2} = \frac{1}{4\pi}\overline{\mathcal{H}^2}$$

In case the first term is nonvanishing the transition is said to be allowed by an electric dipole mechanism, and if the second term is nonvanishing, by a magnetic dipole mechanism.

The oscillator strength of the transition, $n \leftarrow 0$, is defined as

$$f = \frac{B_{n\leftarrow o}}{B_h} = \frac{2m\hbar\nu}{e^2} B_{n\leftarrow o}$$

where B_h is the electric dipole moment matrix element between the first two states of an electron harmonic oscillator with frequency ν.

Singlet-Triplet Transition in Glyoxal

Introduction

In this section the oscillator strength of the lowest singlet-triplet transition in glyoxal, $^3A_u \leftarrow {}^1A_g$, is calculated approximately on the basis of a spin-orbit perturbation of the excited triplet state. The transition is rigorously forbidden in the absence of this perturbation since a change in spin multiplicity from singlet to triplet would cause all matrix elements in the transition probability expression, $B_{n\leftarrow o}$, to vanish. That is, the matrix elements are of the form

$$\langle \psi_s | \Gamma | \psi_\tau \rangle$$

where wavefunctions correspond to singlet and triplet functions, and Γ is the electric dipole or magnetic dipole operator. Thus if Γ does not involve the spin operators S_x, S_y, or S_z, the orthogonality of spin functions causes the matrix to vanish. In case Γ contains

spin operators only, as in the magnetic dipole term, the matrix again would be zero if the singlet and triplet functions correspond to different molecular orbital configurations.

Spin-orbit interaction destroys the exact triplet character of a state and has the effect of mixing with the triplet wavefunction, ψ_T, a small amount of singlet character to give the new wavefunction,

$$\psi_T' = N^{-1}\{\psi_T + \lambda_1\psi_k' + \lambda_2\psi_k^2 + \cdots\}$$

where the ψ_k denote singlet wavefunctions. Thus, since the spin operator S^2 no longer commutes with the Hamiltonian if spin-orbit interactions are included, the wavefunction is not required to an eigenfunction of the total spin.

Spin-orbit energy effects, and consequently the mixing coefficients λ, are generally quite small, and for these reasons the state, ψ_T', will still be referred to as a triplet. Mathematically, however, the singlet-triplet transition is allowed only because the coefficients are nonzero. For example, if only one singlet state is mixed with the triplet, the oscillator strength for the singlet-triplet transition becomes

$$f_{T\leftarrow S} = f_{k\leftarrow S}\,\frac{\nu_{TS}}{\nu_{kS}}\,|\lambda|^2$$

where $f_{k\leftarrow s}$ is the oscillator strength for the singlet-singlet transition, $k\leftarrow s$, ν_{kS} is the frequency of this transition, and ν_{TS} is the frequency of the resulting singlet-triplet transition. The corresponding

result for the case of several singlet states is easily derivable from the $B_{n \leftarrow o}$ transition probability expression.

Estimates of singlet-singlet oscillator strengths from either experimental evidence or general principles are available, and thus the essential objective of this work is a determination of the mixing coefficients λ. The calculation is based on a consideration of the following topics:

a. Spin-orbit Hamiltonian.

b. Quantization of spin.

c. Singlet states.

d. Singlet-triplet interaction.

e. Numerical evaluations.

Hamiltonian

The spin-orbit Hamiltonian for electrons in a molecule may be approximated as a sum of Hamiltonians for individual electrons, in which the interaction of spin with the orbital motion of the same electron is taken into account, but the more random interaction of spin with the orbital motion of other electrons is neglected. The Hamiltonian thus obtained by Bohm (45), and also obtained in Chapter IX by suitable assumptions, is

$$H_{so} = \frac{e\hbar^2}{2m^2c^2} \sum_k (S_k \cdot P_k \times \nabla V_k)$$

where the sum is over all electrons in the molecule, S_k is the spin angular momentum operator for the k^{th} electron in units of $\hbar$,

$$S_k = (S_{xk}, S_{yk}, S_{zk})$$

p_k is the linear momentum in units of $\hbar$, and V is the potential which is due to the presence of all nuclei and other electrons.

The Hamiltonian is readily proved Hermitian by the following use of the adjoint operator definition; however, the main interest here is not a proof of this fact, but rather is a transformation of the Hamiltonian into a more convenient form. Thus, considering only one electron, H_{so} becomes

$$H_{so} = \frac{\sqrt{-1}\, e\hbar^2}{2m^2c^2}\left(h_x S_x + h_y S_y + h_z S_z\right)$$

where

$$h_x = \left(\frac{\partial V}{\partial y}\frac{\partial}{\partial z} - \frac{\partial V}{\partial z}\frac{\partial}{\partial y}\right) \qquad h_y = \left(\frac{\partial V}{\partial z}\frac{\partial}{\partial x} - \frac{\partial V}{\partial x}\frac{\partial}{\partial z}\right) \qquad h_z = \left(\frac{\partial V}{\partial x}\frac{\partial}{\partial y} - \frac{\partial V}{\partial y}\frac{\partial}{\partial x}\right)$$

Matrix elements of individual terms may be transformed as follows using the definition of an adjoint operator, or equivalently by an integration by parts.

$$\begin{aligned}\left\langle \phi_a \middle| \frac{\partial V}{\partial y}\frac{\partial}{\partial z} - \frac{\partial V}{\partial z}\frac{\partial}{\partial y} \middle| \phi_b \right\rangle &= \left\langle \frac{\partial}{\partial y}^{+}\phi_a \middle| V\frac{\partial}{\partial z}\middle|\phi_b\right\rangle - \left\langle \phi_a \middle| V\frac{\partial^2\phi_b}{\partial y\,\partial z}\right\rangle \\ &\quad - \left\langle \frac{\partial}{\partial z}^{+}\phi_a \middle| V\frac{\partial}{\partial y}\middle|\phi_b\right\rangle + \left\langle \phi_a \middle| V\frac{\partial^2\phi_b}{\partial z\,\partial y}\right\rangle \\ &= \int V\left(\frac{\partial\phi_a}{\partial z}\frac{\partial\phi_b}{\partial y} - \frac{\partial\phi_a}{\partial y}\frac{\partial\phi_b}{\partial z}\right)d\tau\end{aligned}$$

where the last step is a consequence of the anti-Hermitian character of $\partial/\partial y$ and $\partial/\partial z$, i.e., $\partial^{+}/\partial y = -\partial/\partial y$, etc.

Corresponding matrix elements for h_y and h_z are

$$\langle \phi_a | h_y | \phi_b \rangle = \int V \left(\frac{\partial \phi_a}{\partial x} \frac{\partial \phi_b}{\partial z} - \frac{\partial \phi_a}{\partial z} \frac{\partial \phi_b}{\partial x} \right) d\tau$$

$$\langle \phi_a | h_z | \phi_b \rangle = \int V \left(\frac{\partial \phi_a}{\partial y} \frac{\partial \phi_b}{\partial x} - \frac{\partial \phi_a}{\partial x} \frac{\partial \phi_b}{\partial y} \right) d\tau$$

Potential Functions

In the present application to glyoxal, an effective potential of the form

$$V = \frac{Z^o e}{r_{o1}} + \frac{Z^c e}{r_{c1}} + \frac{Z^c e}{r_{c2}} + \frac{Z^o e}{r_{o2}}$$

is assumed where r_o and r_c are radial coordinates from the respective oxygen and carbon nuclei, and Z^o and Z^c are effective nuclear charges with values,

$$Z^o = 4.4456$$

$$Z^c = 3.1062$$

The charges are assumed equal to the effective orbital nuclear charges used in Chapter VII which correspond to the best SCF atom parameters. It does not follow necessarily that the effective potential has the same value as the effective nuclear charge, but the assumption should be fairly reliable, and is certainly a logical choice in the absence of more detailed information about the charge distribution.

Quantization of Spin

Electron spin is considered quantized relative to the molecule fixed z axis shown in Figure 5 which passes through both oxygen nuclei

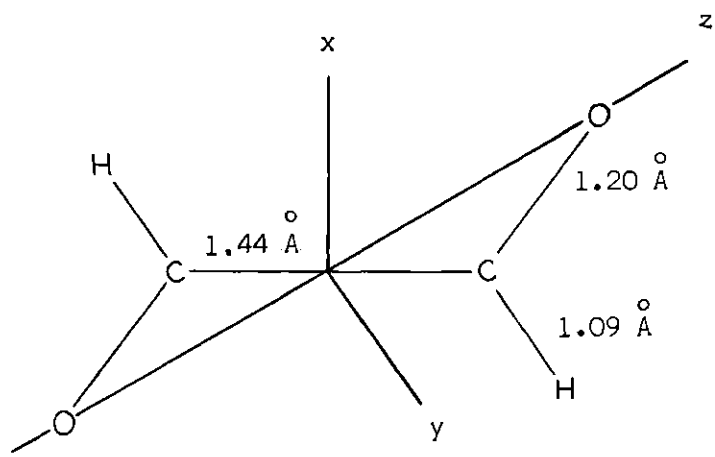

Figure 5. Rotational Axes in Glyoxal

in the planar configuration. The x, y, z coordinate system thus defined, is not the same as the coordinate system used in the symmetry discussion of Chapter VII, but instead is the one which has significance in description of molecular rotation. Subsequently, the coordinate system in Chapter VII is designated as the x', y', z' system, and the coordinate system defined in Figure 5 is designated by x, y, and z. It is convenient to perform computations involving the spatial spin-orbit operators h_x, h_y, and h_z relative to the symmetry axes x', y', z', and therefore to employ the transformation

$$\begin{pmatrix} h_x \\ h_z \\ h_y \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & -\sin\theta \\ 0 & \sin\theta & \cos\theta \end{pmatrix} \begin{pmatrix} h'_z \\ h'_y \\ h'_x \end{pmatrix}$$

where the primed operators have the following definitions and transformation properties relative to the C_{2h} point group.

$$h'_x = \frac{\partial V}{\partial y'}\frac{\partial}{\partial z'} - \frac{\partial V}{\partial z'}\frac{\partial}{\partial y'} \qquad (b_g)$$

$$h'_y = \frac{\partial V}{\partial z'}\frac{\partial}{\partial x'} - \frac{\partial V}{\partial x'}\frac{\partial}{\partial z'} \qquad (b_g)$$

$$h'_z = \frac{\partial V}{\partial x'}\frac{\partial}{\partial y'} - \frac{\partial V}{\partial y'}\frac{\partial}{\partial x'} \qquad (a_g)$$

The C_{2h} character table is given in Chapter VII.

Singlet States

It is now of interest to examine which singlet states can be mixed by the a_g and b_g spin-orbit operators with the triplet state,

$$\psi_5 \rightarrow \psi_3 \quad (\pi^* \leftarrow n) \quad {}^3A_u$$

where the notation used is that of Chapter VII. These states are listed in Table 7. There are two notable omissions from the table. The first is the ground state which, because it has symmetry A_g, cannot be mixed with the ${}^3A_u$ state. The second omission is the singlet state corresponding to the same molecular orbital configuration as the triplet; mixing in this case is rigorously forbidden as may be proved from the Hermitian property of the spin-orbit operator. If mixing were to occur, the matrix element would be

$$\langle \psi_a | H_{so} | \psi_a \rangle$$

and hence would be real since the element is a diagonal one. However, all spin-orbit matrix elements are pure imaginary if the functions are real, and thus the matrix must be zero.

Mathematical Treatment

Finally, it is necessary to consider the mathematical treatment of the spin-orbit perturbation. The triplet state is three-fold degenerate in the absence of spin interactions and corresponds to the three components with eigenvalues 0 and ±1 of the spin operator S_z,

$$\psi_{+1} = 2^{-\frac{1}{2}} \{ \psi_3(1)\psi_5(2) - \psi_5(1)\psi_3(2) \} \alpha(1)\alpha(2)$$

$$\psi_0 = 2^{-1} \{ \psi_3(1)\psi_5(2) - \psi_5(1)\psi_3(2) \} \{ \alpha(1)\beta(2) + \alpha(2)\beta(1) \}$$

Table 7. Excited States of Glyoxal

	Excited State[a]	Symmetry	Observed Transition[b] (λ)	Energy[c] (ev.)
0.	$\psi_5 \rightarrow \psi_3$ ($\pi^* \leftarrow n$)	^3A_u	5000 Å[d]	2.48
1.	$\psi_2 \rightarrow \psi_3$ ($\pi^* \leftarrow \pi$)	^1B_u	1750[e]	7.08
2.	$\psi_5 \rightarrow \psi_{10}$ ($\sigma^* \leftarrow n$)	^1B_u	2050[e]	6.05
3.	$\psi_5 \rightarrow \psi_{14}$ ($\sigma^* \leftarrow n$)	^1B_u	-	12[f]
4.	$\psi_7 \rightarrow \psi_3$ ($\pi^* \leftarrow \sigma$)	^1A_u	-	18[f]
5.	$\psi_{11} \rightarrow \psi_3$ ($\pi^* \leftarrow \sigma$)	^1A_u	-	20[f]
6.	$\psi_9 \rightarrow \psi_3$ ($\pi^* \leftarrow \sigma$)	^1A_u	-	20[f]

a. The notation of Chapter VII is used.

b. Wavelength of the observed transition from the ground electronic state.

c. The energy is defined relative to a ground state value of zero.

d. W. H. Eberhardt and H. Renner (35).

e. A. D. Walsh (46).

f. Estimated energies are based on the results of a SCF calculation of formaldehyde by Goodfriend, Birss, and Duncan (40).

$$\psi_{-1} = 2^{-\frac{1}{2}} \left\{ \psi_3(1)\psi_5(2) - \psi_5(1)\psi_3(2) \right\} \beta(1)\beta(2)$$

where the complete determinant wavefunction of Chapter VII is not used, but instead only the open shell configuration is indicated. A justification of this two-electron formulation is given in Appendix VII. Since the three triplet components are degenerate, it is not necessarily correct to apply nondegenerate perturbation theory in order to determine the mixing with singlet states, but a variational solution is inconvenient since a large number of states are involved. It is shown in Appendix V, however, that nondegenerate perturbation theory gives the correct result for the overall transition probability to the triplet, but not for the transition probability to a specified component. It is the overall transition probability that is of interest in this work.

Thus the application of nondegenerate perturbation theory to the three triplet components gives

$$\psi'_{+1} = \psi_{+1} + \sum_k a_k \phi_k$$

$$\psi'_{0} = \psi_{0} + \sum_k b_k \phi_k$$

$$\psi_{-1} = \psi_{-1} + \sum_k c_k \phi_k$$

where ϕ_k is the k^{th} singlet state in Table 7,

$$\phi_k = 2^{-1} \left\{ \psi_a(1)\psi_b(2) + \psi_b(1)\psi_a(2) \right\} \left\{ \alpha(1)\beta(2) - \alpha(2)\beta(1) \right\}$$

and ψ_a and ψ_b denote molecular orbitals of the open shell configuration. The coefficients are defined as follows,

$$a_k = \langle \Phi_k | H_{so}^1 + H_{so}^2 | \psi_{+1} \rangle (E_T - E_k)^{-1}$$

$$b_k = \langle \Phi_k | H_{so}^1 + H_{so}^2 | \psi_0 \rangle (E_T - E_k)^{-1}$$

$$c_k = \langle \Phi_k | H_{so}^1 + H_{so}^2 | \psi_{-1} \rangle (E_T - E_k)^{-1}$$

where the superscripts on H_{so} refer to electrons 1 and 2, and $E_T - E_K$ is the difference in energy of the triplet and singlet states.

The matrix elements may be expanded using the following one-electron spin identities, where $\gamma = 2^{-1/2}(\alpha(1)\beta(2) - \alpha(2)\beta(1))$.

$$S_x\alpha = \tfrac{1}{2}\beta \qquad S_y\beta = -\tfrac{i}{2}\alpha$$

$$S_x\beta = \tfrac{1}{2}\alpha \qquad S_z\beta = -\tfrac{1}{2}\beta$$

$$S_y\alpha = \tfrac{i}{2}\beta \qquad S_z\alpha = \tfrac{1}{2}\alpha$$

$$\langle \alpha(1)\alpha(2) | S_{x1} | \gamma \rangle = -2^{-3/2}$$

$$\langle \beta(1)\beta(2) | S_{x1} | \gamma \rangle = 2^{-3/2}$$

$$\langle \alpha(1)\alpha(2) | S_{y1} | \gamma \rangle = i2^{-3/2}$$

$$\langle \beta(1)\beta(2) | S_{y1} | \gamma \rangle = i\,2^{-3/2}$$

$$\langle \alpha(1)\alpha(2) | S_{z1} | \gamma \rangle = 0$$

$$\langle \beta(1)\beta(2) | S_{z1} | \gamma \rangle = 0$$

$$\langle \alpha(1)\beta(2) + \alpha(2)\beta(1) | S_{x1} | \gamma \rangle = 0$$

$$\langle \alpha(1)\beta(2) + \alpha(2)\beta(1) | S_{y1} | \gamma \rangle = 0$$

$$\langle \alpha(1)\beta(2) + \alpha(2)\beta(1) | S_{z1} | \gamma \rangle = 2^{-1/2}$$

Thus, matrix elements in the a_k, b_k, and c_k expressions can be reduced to integrals over simple one electron molecular orbitals,

$$\langle \psi | h | \psi_k \rangle$$

where h represents h_x, h_y, or h_z, and ψ and ψ_k denote molecular orbitals of the triplet and singlet states, respectively.

Numerical Evaluations

Spin-orbit interaction integrals were evaluated using the Gaussian function expansions of atomic orbitals discussed in Chapter VII. This application illustrates the utility of Gaussian function formulations since multicenter potential integrals involving the derivatives of hydrogen-like orbitals are difficult to evaluate, and consequently, have been neglected or roughly estimated in most spin-orbit treatments.

The contribution of multicenter integrals to the total spin-orbit interaction is not known in general, but in glyoxal, the results of this work indicate a contribution only approximately one-tenth of the total. This conclusion does not necessarily extend to other molecules since, for example in benzene, McClure has shown that all one center contributions vanish if only π and π^* states are considered.

A test of the accuracy of the Gaussian function approximations in the evaluation of spin-orbit interaction integrals is possible in the case of one center integrals since these are easily evaluated using hydrogen-like orbitals. The exact value of the integral involving $2p_x$ and $2p_y$ orbitals with equal scale factors, Z, and the spin-orbit operator, h_z, is

$$\langle 2p_x | h_z | 2p_y \rangle = \int \frac{Z}{r} \left(\frac{\partial 2p_y}{\partial y} \frac{\partial 2p_x}{\partial x} - \frac{\partial 2p_y}{\partial x} \frac{\partial 2p_x}{\partial y} \right) d\tau$$

$$= \frac{1}{24} \frac{Z^4}{a_o^3}$$

where a_o is the Bohr radius. The corresponding value obtained using the Gaussian 2p orbital approximation with three terms in each lobe function is

$$0.0396715 \frac{Z^4}{a_o^3}$$

which differs by five per cent from the exact value.

This error is not significant in the order of magnitude calculation performed in this work; therefore, all integrals were evaluated using Gaussian function expansions even though exact one center values were available. Integrals over molecular orbitals are given in Table 8, and integrals over individual atomic orbitals are included in Appendix IV. Results are reported in atomic units where

$$\langle \psi | \frac{ieh^2}{2m^2c^2} h | \psi \rangle =$$

$$\frac{i\hbar^2}{2m^2c^2a_o^2}\langle\psi|\hat{h}|\psi_k\rangle_{a.u.} = \frac{i\alpha^2}{2}\langle\psi|\hat{h}|\psi_k\rangle_{a.u.}$$

in which $\hat{h}$ represents h_x, h_y, or h_z, and α is the fine structure constant, $\alpha = 7.2973 \times 10^{-3}$.

A numerical evaluation of the coefficients a_k, b_k, and c_k defined in the previous section is now possible based on the matrix elements in Table 8, the singlet state energies given in Table 7, and the previously obtained integrals over spin functions. Thus,

$$a_k = \langle\phi_k|H'_{so} + H^2_{so}|\psi_{+1}\rangle\,(E_T - E_k)^{-1}$$

$$= \left\{-2^{-3/2}\langle\psi_k|h_x|\psi\rangle + i2^{-3/2}\langle\psi_k|h_y|\psi\rangle\right\}(E_T - E_k)^{-1}$$

$$b_k = \tfrac{1}{2}\langle\psi_k|h_z|\psi\rangle\,(E_T - E_k)^{-1}$$

$$c_k = \left\{2^{-3/2}\langle\psi_k|h_x|\psi\rangle + i2^{-3/2}\langle\psi|h_y|\psi_k\rangle\right\}(E_T - E_k)^{-1}$$

where the difference in energy of the individual components of the triplet is neglected, and functions ψ and ψ_k refer to molecular orbitals of the triplet and singlet states, respectively.

It is convenient to consider each singlet state separately in the computation of the oscillator strength of the singlet-triplet transition. From the derivation in Appendix V, the contribution of one singlet state, k, to the oscillator strength is

$$f_{T\leftarrow S} = f_{k\leftarrow S}\,\frac{\nu_{TS}}{\nu_{KS}}\left\{|a_k|^2 + |b_k|^2 + |c_k|^2\right\}$$

Table 8. Matrix Elements of Spin-Orbit Operators

	h_x[a]	h_y	h_z
$\langle \psi_5 \vert h \vert \psi_2 \rangle$	0	4.0843	-10.2729
$\langle \psi_5 \vert h \vert \psi_7 \rangle$	4.7159	0	0
$\langle \psi_3 \vert h \vert \psi_{10} \rangle$	0	-1.9537	1.3097
$\langle \psi_5 \vert h \vert \psi_{11} \rangle$	-8.9025	0	0
$\langle \psi_3 \vert h \vert \psi_{14} \rangle$	0	1.9758	0.8902

	h'_x	h'_y	h'_z
$\langle \psi_5 \vert h \vert \psi_2 \rangle$	9.5639	-5.5453	0
$\langle \psi_5 \vert h \vert \psi_7 \rangle$	0	0	4.7159
$\langle \psi_3 \vert h \vert \psi_{10} \rangle$	-2.3453	-0.1795	0
$\langle \psi_5 \vert h \vert \psi_{11} \rangle$	0	0	-8.9025
$\langle \psi_3 \vert h \vert \psi_{14} \rangle$	1.0018	1.9217	0

a. Values are reported in atomic units, 1 a.u. = 27.206 ev.

where s denotes the ground singlet state, $f_{k \leftarrow s}$ is the oscillator strength for the singlet-singlet transition, $k \leftarrow s$, ν_{ks} is the frequency of this transition, and ν_{Ts} is the frequency of the resulting singlet-triplet transition. It is emphasized that the oscillator strength calculated in this manner refers to the overall transition probability to the triplet, and not to the transition probability to an individual component.

Contributions of individual singlet states listed in Table 7 are calculated below.*

(1.) $\psi_2 \rightarrow \psi_3$ $(\pi^* \leftarrow \pi)$ ^1A_u

$$f_{T \leftarrow S} = f_{1 \leftarrow S} \left\{\frac{a^4}{4}\right\} \frac{0.0911}{0.260} \left\{\frac{(4.0843)^2 + (10.2729)^2}{(4)(0.169)^2}\right\}$$

$$= f_{1 \leftarrow S} \, (2.655 \times 10^{-7})$$

$$= 0.797 \times 10^{-7} \qquad (\text{for } f_{1 \leftarrow S} = 0.3)^{\ddagger}$$

(2.) $\psi_5 \rightarrow \psi_{10}$ $(\sigma^* \leftarrow n)$ ^1B_u

$$f_{T \leftarrow S} = f_{2 \leftarrow S} \left\{\frac{a^4}{4}\right\} \frac{0.0911}{0.222} \left\{\frac{(1.9537)^2 + (1.3097)^2}{(4)(0.131)^2}\right\}$$

$$= f_{2 \leftarrow S} \, (2.34 \times 10^{-8})$$

$$< 2.34 \times 10^{-9} \qquad (\text{for } f_{2 \leftarrow S} < 0.1)$$

---

*All energies are expressed in atomic units.

‡Oscillator strength estimates are discussed at the conclusion of the computations.

(3.) $\psi_5 \rightarrow \psi_{14}$ $(\sigma^* \leftarrow n)$ ^1B_u

$$f_{T \leftarrow S} = f_{3 \leftarrow S} \left\{\frac{\alpha^4}{4}\right\} \frac{0.0911}{0.441} \left\{\frac{(1.9758)^2 + (0.8902)^2}{(4)(0.349)^2}\right\}$$

$$= f_{3 \leftarrow S} \, (1.41 \times 10^{-9})$$

$$< 1.41 \times 10^{-10} \qquad (\text{for } f_{3 \leftarrow S} < 0.1)$$

(4.) $\psi_7 \rightarrow \psi_3$ $(\pi^* \leftarrow n)$ ^1A_u

$$f_{T \leftarrow S} = f_{4 \leftarrow S} \left\{\frac{\alpha^4}{4}\right\} \frac{0.0911}{0.662} \left\{\frac{(4.7159)^2}{(4)(0.570)^2}\right\}$$

$$= f_{4 \leftarrow S} \, (1.67 \times 10^{-9})$$

$$= 1.67 \times 10^{-10} \qquad (\text{for } f_{4 \leftarrow S} < 0.1)$$

(5.) $\psi_{11} \rightarrow \psi_3$ $(\pi^* \leftarrow \sigma)$ ^1A_u

$$f_{T \leftarrow S} = f_{5 \leftarrow S} \left\{\frac{\alpha^4}{4}\right\} \frac{0.0911}{0.735} \left\{\frac{(8.9025)^2}{(4)(0.643)^2}\right\}$$

$$= f_{5 \leftarrow S} \, (4.21 \times 10^{-9})$$

$$< 4.21 \times 10^{-10} \qquad (\text{for } f_{5 \leftarrow S} < 0.1)$$

(6.) $\psi_9 \rightarrow \psi_3$ $(\pi^* \leftarrow \sigma)$

The contribution of this state to the singlet-triplet oscillator strength is negligible since no one center spin-orbit interaction integrals occur.

Estimates of oscillator strengths for the singlet-singlet transitions are based on Sidman's estimates for formaldehyde (47) in which the $\pi^* \leftarrow \pi$ transition is assigned the value 0.3, and all other transitions are assumed to have values that are less by a factor of ten. Despite these rough estimates, the above calculation shows conclusively that the most significant contribution to the oscillator strength of the singlet-triplet transition is due to the singlet state corresponding to a $\pi^* \leftarrow \pi$ promotion.

It is important to recognize, however, that the calculation is highly approximate since molecular orbitals are not at all well determined. In addition, the possibility of transitions to the Rydberg states involving 3p and 3d orbitals has been ignored. Such transitions, at least on the basis of formaldehyde estimates, should correspond to energies around 10 ev., and should have relatively strong oscillator strengths. The magnitude of the spin-orbit interaction energy, however, should be less than occurs in 2p - 2p interactions.

Neglecting other effects, the final estimate of the oscillator strength of the singlet triplet-transition is

$$f = 0.797 \times 10^{-7}$$

which is of the same order of magnitude as the value, $f = 1.5 \times 10^{-7}$, obtained by Sidman for the corresponding $\pi^* \leftarrow n$ transition in formaldehyde (47). The agreement is not surprising since the only innovations in the present work are the inclusion of all multicenter spin-orbit interaction integrals, and the use of Gaussian functions.

Magnetic Dipole Transition

A second possible transition in the 5000 Å region of the glyoxal spectrum corresponds to a magnetic dipole transition from the ground state to the singlet state with the following molecular orbital configuration

$$\psi_9^2\ \psi_{11}^2\psi_{12}^2\psi_7^2\ \psi_8^2\ \psi_1^2\ \psi_2^2\ \psi_5^2\ \psi_6\psi_3$$

using the notation of Chapter VII. Thus, the transition corresponds to a promotion of the $\pi^* \leftarrow n$ type,

$$\psi_6 \rightarrow \psi_3 \quad (^1B_g)$$

where the overall symmetry of the state is indicated as B_g. This transition is symmetry forbidden by an electric dipole mechanism, but is allowed by a magnetic dipole mechanism; as a consequence, the transition is of relatively low intensity.

Since the transition is likely in the same region of the spectrum as the singlet-triplet transition, a calculation of the oscillator strength is of interest. Using results from the section on radiation theory, the transition probability expression,

$$B_{M-S} = \frac{2\pi}{3\hbar^2}\left|\langle\psi_M\left|\frac{e}{2mc}\sum_k \underline{i}\,M_x + \underline{j}\,M_y + \underline{k}\,M_z\right|\psi_S\rangle\right|^2$$

is obtained where ψ_M and ψ_S denote wavefunctions for the excited singlet state and the ground state, respectively, and the summation is over all electrons, k. The operator $\underline{i}\,M_x + \underline{j}\,M_y + \underline{k}\,M_z$ is the angular momentum operator r x p.

Expansion of the matrix element for two electron wavefunctions, ψ_M and ψ_S representing open shell configurations, gives

$$B_{M\leftarrow S} = \frac{2\pi}{3h^2} \left| \langle \psi_6 | -\frac{\sqrt{2}e}{2mc} (r \times p) | \psi_3 \rangle \right|^2$$

where

$$\psi_6 = \frac{q_1 - q_2}{\sqrt{2}}$$

$$\psi_3 = (p_1^o - p_1^c - p_2^c + p_2^o)(1.8723)^{-1}$$

and q and p represent the oxygen 2p orbitals previously defined.

The following matrix elements of r x p were obtained using the Gaussian expansions of 2p atomic orbitals given in Chapter VII.

$$\langle q_1 | r \times p | p_1^o \rangle = 0.86601\ \underline{i} - 0.5\ \underline{j}$$

$$\langle q_1 | r \times p | p_1^c \rangle = 0.19928\ \underline{i} - 0.11506\ \underline{j}$$

$$\langle q_1 | r \times p | p_2^c \rangle = -0.019816\ \underline{i} - 0.035294\ \underline{j}$$

$$\langle q_1 | r \times p | p_2^o \rangle = -0.000034\ \underline{i} - 0.000047\ \underline{j}$$

Thus

$$\left| \langle \psi_6 | -\frac{\sqrt{2}e}{2mc} (r \times p) | \psi_3 \rangle \right|^2 = \left| \beta \left(\frac{2}{1.8723} \right) (0.68651\ \underline{i} - 0.3497\ \underline{j}) \right|^2$$

$$= 0.6774\ \beta^2$$

where β is the Bohr magneton, $\beta = eh/4\pi mc$. The corresponding oscillator strength of the transition is

$$f = 5.46 \times 10^{-7}$$

which is larger by a factor of seven than the oscillator strength of the singlet-triplet transition calculated in the previous section.

The absorption spectrum of glyoxal in the region around 5000 Å, therefore, is likely due to both magnetic dipole and singlet-triplet transitions. However, according to current theory, only the singlet-triplet transition is responsible for the observed magnetic rotation spectrum.

CHAPTER IX

ROTATIONAL FINE STRUCTURE OF THE TRIPLET STATE AND MAGNETIC INTERACTIONS

Introduction

The general theoretical problem of describing the triplet excited state of glyoxal is one of determining the eigenvalues and eigenfunctions of the Hamiltonian

$$H = H_e + H_n + H_{so} + H_{ss} + H_{sn} + H_f$$

in which individual Hamiltonians refer to electronic, nuclear motion, spin-orbit, spin-spin, spin-nuclear-motion, and higher order interaction energies, respectively. The Hamiltonian for nuclear motion may be separated approximately into vibrational and rotational contributions,

$$H_n = H_v + H_r$$

corresponding to a neglect of translational motion. Solutions to the major part of the Hamiltonian,

$$H = H_e + H_v + H_r$$

are then obtainable within the limitations of the Born-Oppenheimer approximation (48) as a product of electronic, vibrational, and rotational wavefunctions,

$$\psi = \psi_e \psi_v \psi_r$$

The remaining terms in the Hamiltonian which are due to magnetic interactions involving electron spin, exhibit relatively small energy effects as is evidenced by a splitting of individual rotational lines. One of the main objectives of this chapter is a theoretical description of these interactions in the triplet state of glyoxal.

The Triplet Electronic State

Wavefunctions for the three triplet components of glyoxal constructed using the LCAO-MO theory of Chapter VII are

$$\psi_{+1} = 2^{-1/2}\left\{\psi_5(1)\psi_3(2) - \psi_3(1)\psi_5(2)\right\}\alpha(1)\alpha(2)$$

$$\psi_0 = 2^{-1}\left\{\psi_5(1)\psi_3(2) - \psi_3(1)\psi_5(2)\right\}\alpha(1)\beta(2) + \alpha(2)\beta(1)$$

$$\psi_{-1} = 2^{-1/2}\left\{\psi_5(1)\psi_3(2) - \psi_3(1)\psi_5(2)\right\}\beta(1)\beta(2)$$

where only the open shell configuration, and not the complete determinantal wavefunction, is given. It may be shown by a proof similar to the one given in Appendix VII that the closed shell electrons do not contribute for the operators considered here. The molecular orbitals ψ_5 and ψ_3 are those used previously, and refer, respectively, to the nonbonding oxygen orbitals

$$\psi_5 = (q_1 + q_2)2^{-1/2}$$

and the lowest antibonding π molecular orbital

$$\psi_3 = (p_1^o - p_1^c - p_2^c + p_2^o) N_3^{-1}$$

Spin functions α and β refer to the molecule fixed axes shown in Figure 5 of Chapter VIII. This introduction of pure spin states is a temporary one which is correct only for the nonrotating molecule.

One result that is of interest, despite the fact that molecular rotation tends to destroy its significance, is the spin-spin splitting determined by the operator,

$$H_{ss} = 0.26 \{ 3S_z^2 - S^2 \}$$

where $S_z = S_{z1} + S_{z2}$ in units of $\hbar$, and 0.26 is an evaluated constant in cm^{-1} which is considered in detail later. The zero component thus is split from the ± 1 components by 0.78 cm^{-1}, while the latter two components remain degenerate.

The Rotating Molecule

Rotation of the glyoxal molecule for the planar framework of nuclei shown in Figure 5 is well characterized as that of a prolate symmetric rotor with Hamiltonian

$$H_R^o = AN_x^2 + BN_y^2 + CN_z^2$$

where N_x, N_y, and N_z are rotational angular momentum operators defined relative to the axes indicated in the figure, and $A = \hbar^2/2I_x$,

$B = \hbar^2/2I_y$, and $C = \hbar^2/2I_z$ in terms of moments of inertia about the x, y, and z axes.* Neglecting asymmetry in the geometry of glyoxal gives $A \approx B \approx 0.158\ cm^{-1}$ and $C \approx 1.9\ cm^{-1}$. Corresponding energy levels of the prolate rotor are given by

$$E = \frac{A+B}{2}\left[N(N+1) - K^2\right] + CK^2$$

where N is the total rotational angular momentum quantum number and K denotes the quantized projection of the total rotational angular momentum on the figure axis, z. Actually N consists of rotational plus orbital contributions, but the latter is not quantized in a nonlinear molecule.

A description of triplet state energy levels based on the assumption of no interaction between spin and rotational angular momenta and neglecting spin-orbit interaction is that of spin-spin splittings superimposed on the symmetric top energy levels. In general, however, spin-rotational interactions are not negligible and a more detailed treatment is required.

Spin-rotational interactions have been treated by Van Vleck (51) on the basis of an angular momentum coupling scheme in which the rotational, orbital, and spin momenta are coupled to form a resultant total angular momentum J, which is quantized in the absence of directional external fields. Quantization of J precludes a rigorous quantization

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*The symbols A and C are interchanged in the conventional notation for a prolate rotor, but the above notation is retained in order to facilitate reference to Van Vleck's treatment of coupling of angular momenta in molecules (51).

of both spin and rotational momenta, and thus it is possible to retain either the previous spin description or the rotational description, but not both. The former case corresponds to a Hund's case (a) representation and the latter to Hund's case (b).

The remainder of this chapter is devoted to a calculation of magnetic interactions in the triplet state of glyoxal using Van Vleck's general theory (51). Interaction constants are evaluated using approximate electronic wavefunctions expanded as linear combinations of Gaussian functions. Since explicit formulas for interaction constants are not given by Van Vleck, certain parts of his derivation are reconsidered.

Magnetic Interactions in the Triplet State

Approximate eigenvalues of the Hamiltonian,

$$H = H_r + H_{ss} + H_{so} + H_{sn}$$

are determined using matrix elements of a Hund's case (b) representation diagonal in the quantum numbers K and N. Higher order interactions, H_f, such as nuclear spin interactions etc. are neglected. The case (b) basis is characterized by the quantum numbers

$$J, M, S, N, K$$

where J represents the total angular momentum of the molecule, M the projection of the total angular momentum on a space-fixed Z axis, S the total spin angular momentum, N the total angular momentum exclusive

of spin, and K its projection on the molecule-fixed z axis. Corresponding operators defined relative to molecule-fixed axes are

$$J_x , J_y , J_z , S_x , S_y , S_z$$

$$N_x = J_x - S_x , \quad N_y = J_y - S_y , \quad N_z = J_z - S_z$$

The total spin is only approximately a good quantum number since spin-orbit interaction causes some singlet-triplet mixing.

Since the symmetric rotor Hamiltonian constitutes the major part of H, the quantum numbers N and K roughly characterize the energy levels, and the effect of magnetic interactions is only to split each rotational level into sublevels corresponding to the three different values of J.

$$J = N$$

$$N = N + 1$$

$$J = N - 1$$

The occurrence of off-diagonal matrix elements between states of different N implies that N is not rigorously a good quantum number. However, these matrix elements are proportional to magnetic interaction constants, plus a term representing the departure from a pure symmetric rotor geometry, and consequently, are of secondary importance.

The following rotational and magnetic interaction Hamiltonians are given by Van Vleck (51).

Rigid rotation:

$$H_r = A(J_x - S_x - L_x)^2 + B(J_y - S_y - L_y)^2 + C(J_z - S_z - L_z)^2$$

Spin-spin interaction of two electrons:

$$H_{ss} = g^2\beta^2 r_{12}^{-5}\left\{ r_{12}^2 (S_1 \cdot S_2) - 3(S_1 \cdot \vec{r}_1 - \vec{r}_2)(S_2 \cdot \vec{r}_1 - \vec{r}_2)\right\}$$

Spin-orbit interaction:

$$H_{so} = g\beta/c \sum_k^{nuc} \sum_j^{elec} Z_k e\, r_{jk}^{-3} \left\{ (\vec{r}_j - \vec{r}_k) \times \tfrac{1}{2}\vec{v}_j \right\} \cdot S_j$$

$$+ g\beta/c \sum_{j<l}^{elec} (-e r_{jl}^{-3}) \left\{ (\vec{r}_j - \vec{r}_l) \times (\tfrac{1}{2}\vec{v}_j - \vec{v}_l) \right\} \cdot S_j$$

Spin-nuclear-motion interaction:

$$H_{so} = g\beta/c \sum_k^{nuc} \sum_j^{elec} (Z_k e\, r_{jk}^{-3}) \left\{ (\vec{r}_j - \vec{r}_k) \times (-\vec{v}_k) \right\} \cdot S_j$$

where $\vec{r}$ and $\vec{v}$ denote positions and velocities, respectively, Z_k is the atomic number of the k^{th} nucleus, S is the spin angular momentum operator, $S = (S_x, S_y, S_z)$, and e, c, β, and g denote the electronic charge, velocity of light, Bohr magneton, and electron g factor respectively.

Expansion of H_r gives

$$H_r = AN_x^2 + BN_y^2 + CN_z^2 - 2AL_xN_x - 2BL_yN_y - 2CL_zN_z$$

$$+ AL_x^2 + BL_y^2 + CL_z^2$$

where $N_x = J_x - S_x$, etc. The last term which acts only as a perburbation of the already poorly described electronic state is not responsible for any splittings of energy levels. It will subsequently be omitted.

Expansion of the spin-spin Hamiltonian gives

$$H_{ss} = -g^2\beta^2/4 \{ 6x_{12}y_{12}\,(S_xS_y + S_yS_x) \quad + 6y_{12}z_{12}\,(S_yS_z + S_zS_y)$$

$$+ 6x_{12}z_{12}\,(S_xS_z + S_zS_x) \quad + 3\,(x_{12}^2 - y_{12}^2)(S_x^2 - S_y^2)$$

$$+ (3z_{12}^2 - r_{12}^2)(3S_z^2 - S^2)\} \, r_{12}^{-5}$$

where the following identity has been used in order to obtain a final formula in terms of total spin

$$\langle\psi|S_{x1}S_{y2} + S_{y1}S_{x2}|\psi\rangle \quad = \quad \tfrac{1}{2}\,\langle\psi|S_xS_y + S_yS_x|\psi\rangle$$

where $S_x = S_{x1} + S_{x2}$, $\quad S_y = S_{y1} + S_{y2}$.

Similar identities apply to the other indicated groupings of spin operators.

An expression for the spin-nuclear-motion Hamiltonian may be obtained using nuclear velocities determined from the rotational description

$$v_k = \left(\frac{N_x}{I_x}, \frac{N_y}{I_y}, \frac{N_z}{I_z}\right) \times r_k$$

where r_k is the radius vector from the center of mass of the molecule to the k^{th} nucleus. The result is

$$H_{sn} = -g\beta/c \sum_{k}^{nuc} \sum_{j}^{elec} Z_k e r_{jk}^{-3} \left\{ S_x N_x \left(Y_k Y_{jk} + Z_k Z_{jk}\right) I_x^{-1} \right.$$

$$+ S_y N_y \left(Z_k Z_{jk} + X_k X_{jk}\right) I_y^{-1} \quad + \quad S_z N_z \left(X_k X_{jk} + Y_k Y_{jk}\right) I_z^{-1}$$

$$+ S_x N_x \left(-X_k Y_{jk} I_y^{-1}\right) \quad + \quad S_x N_z \left(-X_k Z_{jk} I_z^{-1}\right)$$

$$+ S_y N_z \left(-Y_k Z_{jk} I_z^{-1}\right) \quad + \quad S_y N_x \left(-Y_k X_{jk} I_x^{-1}\right)$$

$$\left. + S_z N_x \left(-Z_k X_{jk} I_x^{-1}\right) \quad + \quad S_z N_y \left(-Z_k Y_{jk} I_y^{-1}\right) \right\}$$

The only terms in H_{sn} which are diagonal in the quantum numbers K and N in a Hund's case (b) representation are $S_x N_x$, $S_y N_y$, and $S_z N_z$.

The complete spin-orbit Hamiltonian is not used, but instead H_{so} is replaced by

$$H_{so} = g\beta/c \sum_{k}^{nuc} \sum_{j}^{elec} Z_k e r_{jk}^{-3} \left\{ \left(\vec{r}_j - \vec{r}_k\right) \times \tfrac{1}{2} v_j \right\} \cdot S_j$$

where Z_k is an effective nuclear charge for the k^{th} nucleus which is considered screened to account for the presence of other electrons. For a two electron system,

$$H_{so} = (h_{x1}, h_{y1}, h_{z1}) \cdot S_1 + (h_{x2}, h_{y2}, h_{z2}) \cdot S_2$$

where

$$h_1 = (h_{x1}, h_{y1}, h_{z1}) = g\beta/2mc \sum_{k}^{nuc} S_1 \cdot (\nabla V_k \cdot P_1)$$

and

$$V_k = Z_k e / r_{k1}$$

Both the spin orbit operator and the operator,

$$-2A L_x N_x - 2B L_y N_y - 2C L_z N_z$$

are nondiagonal in electronic quantum number, and have an effect only through higher electronic states. Mixing with the ground state is forbidden by symmetry in both cases. All other terms in the expanded Hamiltonian have nonvanishing matrix elements diagonal in the electronic quantum number and hence exhibit a first order effect.

The remaining problem is the diagonalization of the matrix of the total Hamiltonian.

$$H = H_e + H_v + H_r + H_{so} + H_{ss} + H_{sn}$$

relative to Hund's case (b) basis which will be symbolized by an electronic quantum number n and an angular momentum designation j, where j denotes a particular combination of the quantum numbers J, S, N, K, and M. Equivalently, the problem is one of determining mixings of states caused by magnetic interaction terms in the Hamiltonian. There results the usual set of secular equations and corresponding determinant

$$\begin{vmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} & \cdots \\ H_{21}-ES_{21} & H_{22}-ES_{22} & \vdots \\ & \cdots & \end{vmatrix} = 0$$

where H_{ij} and S_{ij} are the Hamiltonian and overlap matrices, respectively, for the nk basis defined above; eigenvalues, E, correspond to the fine structure energy levels.

The determinant may be simplified by the method of treatment derived in Appendix V in which the effect of higher electronic states is well approximated. The method exhibits many of the properties of the Van Vleck transformation (44), but an exact equivalence has not been shown. Thus, letting m and ℓ denote two different angular momentum states for the triplet state of interest, the determinant becomes

$$\begin{vmatrix} H_{mm}-E-\sum_{k_j}\frac{|H_{mk_j}|^2}{E_{k_j}-E_n} & H_{m\ell}-\sum_{k_j}\frac{H_{mk_j}H_{k_j\ell}}{E_{k_j}-E_n} & \cdots \\ H_{\ell m}-\sum_{k_j}\frac{H_{k_jm}H_{\ell k_j}}{E_{k_j}-E_n} & H_{\ell\ell}-E-\sum_{k_j}\frac{|H_{\ell k_j}|^2}{E_{k_j}-E_n} & \vdots \\ & \cdots & \end{vmatrix} = 0$$

where $H_{m\ell}$ refers to the interaction between states m and ℓ diagonal in the electronic quantum number, i.e., $H_{m\ell}=\langle m|H_{ss}+H_{sn}|\ell\rangle$ and the summed terms involve higher electronic states. The index k_j denotes a particular combination of angular momentum quantum numbers corresponding to an electronic state k.

The summations over states may be performed as follows

$$\sum_{k_j} \frac{H_{mk_j} H_{k_j \ell}}{E_{k_j} - E_n} = \sum_{k}^{elec} \sum_{j}^{mom} \frac{H_{mj}^{(k)} H_{j\ell}^{(k)}}{E_j^{(k)} - E_n}$$

$$= \sum_{k}^{elec} \frac{1}{E_k - E_n} \sum_{j}^{mom} H_{mj}^{(k)} H_{j\ell}^{(k)}$$

where summations over all angular momentum states, j, corresponding to a particular electronic state k are performed initially. The dependence of matrix elements on the electronic state is indicated by a superscript. In the second line it has been assumed that the separation between higher electronic states and the triplet state of interest is large so that

$$E_k - E_n \approx E_{k_j} - E_n$$

for all states j belonging to an electronic state k.

Matrix elements, H_{mk_j} and $H_{k_j \ell}$, are those of the operator

$$H = h_{x_1} S_{x_1} + h_{y_1} S_{y_1} + h_{z_1} S_{z_1} + h_{x_2} S_{x_2} + h_{y_2} S_{y_2} + h_{z_2} S_{z_2}$$
$$-2A (\ell_{x_1} + \ell_{x_2}) N_x - 2B (\ell_{y_1} + \ell_{y_2}) N_y - 2C (\ell_{z_1} + \ell_{z_2}) N_z$$

Several observations are noteworthy. The first is that matrix elements of the type

$$\left\langle \frac{\psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1)}{\sqrt{2}} \middle| \ell_{x_1} + \ell_{x_2} \middle| \frac{\psi_a(1)\psi_c(2) + \psi_a(2)\psi_c(1)}{\sqrt{2}} \right\rangle$$

between triplet and singlet spatial functions are identically zero if ψ_a, ψ_b, and ψ_c are orthogonal, but that triplet-triplet matrix elements are

$$\left\langle \frac{\psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1)}{\sqrt{2}} \middle| \ell_{x1} + \ell_{x2} \middle| \frac{\psi_a(1)\psi_c(2) - \psi_a(2)\psi_c(1)}{\sqrt{2}} \right\rangle$$

$$= \langle \psi_b(1) | \ell_{x1} | \psi_c(1) \rangle$$

Secondly,

$$\left\langle \frac{\psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1)}{\sqrt{2}} \middle| h_{x1}S_{x1} + h_{x2}S_{x2} \middle| \frac{\psi_a(1)\psi_c(2) - \psi_c(1)\psi_a(2)}{\sqrt{2}} \right\rangle$$

$$= \frac{1}{2} \langle \psi_b(1) | h_{x1} | \psi_c(1) \rangle (S_{x1} + S_{x2})$$

$$= \frac{1}{2} \langle \psi_b(1) | h_{x1} | \psi_c(1) \rangle S_x$$

but that $S_{x1} - S_{x2}$ instead of $S_{x1} + S_{x2}$ results in the triplet-singlet case. For these reasons, it is convenient to consider summations over singlet and triplet states separately, and to define effective Hamiltonians

$$H = h_{x1}(S_{x1} - S_{x2}) + h_{y1}(S_{y1} - S_{y2}) + h_{z1}(S_{z1} - S_{z2})$$

for triplet-singlet interactions, and

$$H = h_{x1}S_{x1} + h_{y1}S_{y1} + h_{z1}S_{z1} - 4A\ell_{x1}N_x - 4B\ell_{y1}N_y - 4C\ell_{z1}N_z$$

for triplet-triplet interactions.

Only matrix elements between two triplet states are considered in the following derivation; corresponding results are obtained for the triplet-singlet case. Expansion of

$$\sum_{j}^{mom} H_{mj}^{(k)} H_{jl}^{(k)}$$

gives

$$\sum_{j}^{mom} \Big\{ \langle m|h_{x1}S_x|j\rangle\langle j|h_{x1}S_x|l\rangle + \cdots$$

$$- 4A\left[\langle m|h_{x1}S_x|j\rangle\langle j|l_{y1}N_y|l\rangle + \langle m|l_{y1}N_y|j\rangle\langle j|h_{x1}S_x|l\rangle\right]$$

$$+ 4C^2\langle m|l_{z1}N_z|j\rangle\langle j|l_{z1}N_z|l\rangle + \cdots \Big\}$$

where each product may be further separated into an electronic state part and an angular momentum state part. For example,

$$\sum_{j}^{mom} 4B\langle m|h_{x1}S_x|j\rangle\langle j|l_{y1}N_y|l\rangle$$

$$= 4B\langle n|h_{x1}|k\rangle\langle k|l_{y1}|n\rangle \sum_{j}^{mom} \langle m|S_x|j\rangle\langle j|N_y|l\rangle$$

where n and k are electronic states. The summation equality,

$$\sum_{j}^{mom} \langle m|S_x|j\rangle\langle j|N_y|l\rangle = \langle m|S_x N_y|l\rangle$$

may be proved by expansion of $N_y l$ using the completeness property of the set of angular momentum states.

It is now possible to give a final result for the diagonal and off-diagonal sums in terms of a set of evaluated constants. Thus,

$$\sum_{k_i} \frac{H_{mk_i} H_{k_i l}}{E_{k_i} - E_n} = \langle m | a_1 S_x N_x + a_2 S_y N_y + a_3 S_z N_z + a_4 S_x N_y + a_5 S_x N_z + a_6 S_y N_x + a_7 S_y N_z + a_8 S_z N_x + a_9 S_z N_y + \cdots + S_x S_y + \cdots + N_x N_y | l \rangle \langle l | a_1 S_x N_x + \cdots + a_9 S_z N_y + \cdots | m \rangle$$

where

$$a_1 = -8A \sum_k^{elec} Re \frac{\langle n | h_{x1} | k \rangle \langle k | l_{x1} | n \rangle}{E_k - E_n}$$

$$a_2 = -8B \sum_k^{elec} Re \frac{\langle n | h_{y1} | k \rangle \langle k | l_{y1} | n \rangle}{E_k - E_n}$$

$$\cdots$$

$$a_9 = -8B \sum_k^{elec} Re \frac{\langle n | h_{z1} | k \rangle \langle k | l_{y1} | n \rangle}{E_k - E_n}$$

The sums are properly over all electronic and vibrational states, k, although the notation elec. is used.

The result of the above derivation is of considerable importance since it permits the construction of an effective Hamiltonian which is

very nearly diagonal in the electronic quantum number. The terms in this Hamiltonian are of exactly the same form as obtained previously in the treatment of spin-spin and spin-rotational interactions, and thus it is possible to redefine the constants a_1, a_2, a_3, etc., in the effective Hamiltonian in order to express the combined effect of all magnetic interactions. As a result, the following effective Hamiltonian given by Van Vleck (51) is obtained.

$$H = AN_x^2 + BN_y^2 + CN_z^2 - a_o(N_xS_x + N_yS_y + N_zS_z)$$
$$- a(2N_zS_z - N_xS_x - N_yS_y) - b(N_xS_x - N_yS_y) - c(N_xS_y + N_yS_x)$$
$$- d(N_xS_z + N_zS_x) - e(N_yS_z + N_zS_y) + \alpha(2S_z^2 - S_x^2 - S_y^2)$$
$$+ \beta(S_x^2 - S_y^2) + \gamma(S_xS_y + S_yS_x) + \delta(S_xS_z + S_zS_x) + \varepsilon(S_yS_z + S_zS_y)$$

where A, B, and C are the rotational constants, $A = \hbar^2/2I_x$, etc., and a_o, a, b, ..., ε are evaluated constants. Formulas for these constants which are not given by Van Vleck are obtainable from the derivation presented in this chapter.

Matrix elements of the effective Hamiltonian H are given by Van Vleck for a Hund's case (b) basis, but only the following diagonal one is considered in this work:

$$\langle NK|H|NK\rangle = \tfrac{1}{2}(A+B)[N(N+1)] + [C - \tfrac{1}{2}(A+B)]K^2$$
$$+ 3K^2\alpha\rho + \tfrac{1}{2}(a_o - a_o)R + 3aK^2R[N(N+1)]^{-1} - N(N+1)\alpha\rho$$

where

$$R = N(N+1) + S(S+1) - J(J+1)$$

$$\rho = \frac{3R(R-1) - 4N(N+1)S(S+1)}{2N(N+1)(2N-1)(2N+3)}$$

and J, N, K, and S are the quantum numbers previously defined. Thus, $S = 1$ and $J = N$, $N - 1$, or $N + 1$, and

$$R = N(N+1) - J(J+1) + 2$$

$$\rho = \frac{3R(R-1) - 8N(N+1)}{2N(N+1)(2N-1)(2N+3)}$$

It is seen that the diagonal treatment results in a considerable simplification since only three of the eleven interaction constants contribute. In the following application to glyoxal, these constants are evaluated using the Gaussian function expansion of atomic orbitals given in Chapter VII, and thus the treatment provides an illustration of the utility of Gaussian functions in the evaluation of magnetic interaction energies.

Spin-spin Interaction: The major contribution to the interaction constant α is due to a diagonal spin-spin interaction, and only a small contribution which later is shown to be negligible, is due to the non-diagonal effect of spin-orbit interaction. From the expansion of the spin-spin Hamiltonian, H_{ss}, the expression for α is obtained as

$$\alpha = \left\langle \psi_T \left| -\frac{g^2\beta^2}{4} \left(\frac{3z_{12}^2 - r_{12}^2}{r_{12}^5} \right) \right| \psi_T \right\rangle$$

where β is the Bohr magneton, $eh/4\pi mc$, $g = 2$, and ψ_T is the spatial part of the triplet state wavefunction,

$$\psi_T = 2^{-1/2}\left\{\psi_5(1)\psi_3(2) - \psi_3(1)\psi_5(2)\right\}$$

with

$$\psi_5 = \frac{q_1 + q_2}{\sqrt{2}} \qquad \psi_3 = \left(p_1^o - p_1^c - p_2^c + p_2^o\right)N_3^{-1}$$

using the previously defined notation for atomic orbitals. Since spin-spin interactions diminish as the inverse cube of r_{12}, it is a good approximation to neglect all but the one center contributions to the matrix element. In this case α reduces to

$$\alpha = -\beta^2 N_3^{-2}\left\{\left(q_{\pi_1}(1)\, q_{\pi_1}(2) \,\middle|\, \frac{3z_{12}^2 - r_{12}^2}{r_{12}^5} \,\middle|\, p_1^o(2)\, p_1^o(2)\right) - \left(q_{\pi_1}(1)\, p_1^o(1) \,\middle|\, \frac{3z_{12}^2 - r_{12}^2}{r_{12}^5} \,\middle|\, q_{\pi_1}(2)\, p_1^o(2)\right)\right\}$$

or, in atomic units,

$$\alpha = -\beta^2 a_h^{-3} N_3^{-2}\left\{\left(q_{\pi_1} q_{\pi_1} \,\middle|\, \frac{3z_{12}^2 - r_{12}^2}{r_{12}^5} \,\middle|\, p_1^o p_1^o\right) - \left(q_{\pi_1} p_1^o \,\middle|\, \frac{3z_{12}^2 - r_{12}^2}{r_{12}^5} \,\middle|\, q_{\pi_1} p_1^o\right)\right\}_{a.u.}$$

where a_h is the Bohr radius and $\beta^2 a_h^{-3} = 2.9221$ cm^{-1}/a.u. The integral thus involves the $2p_x$ and $2p_y$ orbitals on the oxygen, and is readily evaluated using the spin-spin interaction formula given in Chapter III. The result is

$$\alpha = \left(-\beta^2 a_h^{-3} N_3^{-2}\right)\left(-3.596 \times 10^{-3} Z_o^3\right)$$

where Z_o is the effective nuclear charge or scale factor of the 2p orbitals. Using $Z_o = 4.4456$ and the previously evaluated normalization constant, $N_3^2 = 3.50528$, gives

$$\alpha = 0.26337 \text{ cm}^{-1}$$

It is significant to compare this result with an experimental value obtained by Rayne (55) from an analysis of the singlet-triplet, $\pi^* \leftarrow n$, spectrum of formaldehyde. A value of $\alpha = 0.25 \text{ cm}^{-1}$ was obtained by fitting the diagonal elements of Van Vleck's formula to the data. Since the excited states of glyoxal and formaldehyde are similar in the respect that they both correspond to a $\pi^* \leftarrow n$ promotion, the value of α is in complete agreement with the theoretical result.

Spin-orbit Interaction: The two remaining interaction constants, a_o and a, depend on the effects of spin-orbit interaction and the interaction of spin with the rotation of the framework of nuclei. Since all terms in the latter interaction contain nuclear velocities as factors, as indicated by the expansion of H_{sn}, this effect is generally less significant, even though it is a diagonal contribution, than the effect of spin-orbit interaction. Further support for this contention is found in Tinkham and Strandberg's calculation on the oxygen molecule in which the spin-nuclear-motion interaction was determined to be only four per cent of the total contribution. Therefore, on the basis of these arguments, only spin-orbit effects are considered in the following application to glyoxal. It is noted, however, that the integrals required

for the evaluation of spin-nuclear-motion interactions can be derived for Gaussian functions by the same technique employed in the spin-orbit derivation.

The first step in the calculation requires an evaluation of the coefficients a_1, a_2, and a_3 in

$$a_1 S_x N_x + a_2 S_y N_y + a_3 S_z N_z$$

where, as previously defined,

$$a_1 = -8A \sum_k^{elec} Re \frac{\langle n|h_{x1}|k\rangle\langle k|l_{x1}|n\rangle}{E_k - E_n}$$

$$a_2 = -8B \sum_k^{elec} Re \frac{\langle n|h_{y1}|k\rangle\langle k|l_{y1}|n\rangle}{E_k - E_n}$$

$$a_3 = -8C \sum_k^{elec} Re \frac{\langle n|h_{z1}|k\rangle\langle k|l_{z1}|n\rangle}{E_k - E_n}$$

where n is the triplet electronic state, and the summations are properly over all electronic and vibrational states k.

The lack of detailed information about the excited states of glyoxal prevents a consideration in this work of spin-orbit interactions with different vibrational states; however, the following comments indicate the general significance of this effect. Consider the spin-orbit matrix element between the triplet state ψ_T and some other state ψ.

$$\langle \psi_T | \begin{matrix} a_q \\ b_q \end{matrix} | \psi \rangle$$

where the symmetry of the spin-orbit operator is indicated as a_g or b_g. Separation of the wavefunctions into electronic and vibrational contributions gives

$$\langle A_u V_T | \begin{matrix} a_g \\ b_g \end{matrix} | \Gamma V \rangle$$

where the triplet electronic state is of symmetry A_u and the other electronic state is of symmetry Γ.

In case V is of the same symmetry as V_T then Γ must be of symmetry A_u or B_u but if the possibility of a different vibrational state V is allowed, it is only necessary that the product $\Gamma \times V$ be A_u or B_u. Thus, the effect of ignoring vibrational considerations is to eliminate interaction with all electronic states except those of symmetry A_u or B_u.

The neglect of different vibrational states given the following result for a_3.

$$a_3 = -8C \sum_k \langle n | h_{z1} | k \rangle \langle k | l_{z1} | n \rangle \, (E_k - E_n)^{-1}$$

$$= -8C \sum_k \left\{ \left\langle \frac{\psi_3(1)\psi_5(2) - \psi_5(1)\psi_3(2)}{\sqrt{2}} \middle| h_{z1} \middle| \frac{\psi_a^k(1)\psi_b^k(2) - \psi_b^k(1)\psi_a^k(2)}{\sqrt{2}} \right\rangle \cdot \right.$$

$$\left. \left\langle \frac{\psi_a^k(1)\psi_b^k(2) - \psi_b^k(1)\psi_a^k(2)}{\sqrt{2}} \middle| l_{z1} \middle| \frac{\psi_3(1)\psi_5(2) - \psi_5(1)\psi_3(2)}{\sqrt{2}} \right\rangle (E_k - E_n)^{-1} \right\}$$

where

$$\left(\psi_a^k(1)\,\psi_b^k(2) - \psi_a^k(2)\,\psi_b^k(1)\right) 2^{-1/2}$$

is an excited triplet state corresponding to the molecular orbital configurations listed in Table 7 of Chapter VIII. The matrix elements reduce to one electron integrals over molecular orbitals as in the spin-orbit calculation in the previous chapter. Numerical values for these integrals which were obtained using the previously defined Gaussian function expansions are given in Table 9 for operators defined relative to rotational axes (x, y, z). Results are tabulated in atomic units where

$$\langle \psi_1 | \ell_z | \psi_2 \rangle = \hbar \langle \psi_1 | \ell_z | \psi_2 \rangle_{a.u.}$$

$$\frac{i\hbar^2 e}{2m^2c^2} \langle \psi_1 | h | \psi_2 \rangle = \frac{i\alpha_f^2}{2} \langle \psi_1 | h | \psi_2 \rangle_{a.u.}$$

and α_f is the fine structure constant, $\alpha_f = 7.29726 \times 10^{-3}$. Substitution of the matrix elements into the expression for a_3, and conversion of the energies given in Table 7 into atomic units gives

$$a_3 = -C\alpha_f^2 \left\{\frac{(10.273)(0.7629)}{0.169} + \frac{(1.3097)(0.2554)}{0.131} + \frac{(0.8902)(0.3074)}{0.349}\right\}$$

$$= -5.10 \times 10^{-3}\ \text{cm}^{-1}$$

Similarly,

$$a_1 = -A\alpha_f^2 \left\{\frac{(4.7159)(0.2357)}{0.571} + \frac{(8.9025)(0.4297)}{0.643}\right.$$

$$= -6.64 \times 10^{-5}\ \text{cm}^{-1}$$

Table 9. Matrix Elements of Spin-Orbit and Orbital Angular Momentum Operators

	$\langle h_x \rangle$	$\langle h_y \rangle$	$\langle h_z \rangle$
$\langle \psi_5 \lvert h \rvert \psi_2 \rangle$	0.0	4.0843	-10.2729
$\langle \psi_5 \lvert h \rvert \psi_7 \rangle$	4.7159	0.0	0.0
$\langle \psi_3 \lvert h \rvert \psi_{10} \rangle$	0.0	-1.9537	1.3097
$\langle \psi_5 \lvert h \rvert \psi_{11} \rangle$	-8.9025	0.0	0.0
$\langle \psi_3 \lvert h \rvert \psi_{14} \rangle$	0.0	1.9758	0.8902
	$\langle \ell_x \rangle$	$\langle \ell_y \rangle$	$\langle \ell_z \rangle$
$\langle \psi_5 \lvert \ell \rvert \psi_2 \rangle$	0.0	0.3345	-0.7629
$\langle \psi_5 \lvert \ell \rvert \psi_7 \rangle$	0.2357	0.0	0.0
$\langle \psi_3 \lvert \ell \rvert \psi_{10} \rangle$	0.0	-0.3244	0.2554
$\langle \psi_5 \lvert \ell \rvert \psi_{11} \rangle$	-0.4297	0.0	0.0
$\langle \psi_3 \lvert \ell \rvert \psi_{14} \rangle$	0.0	0.2542	0.3074

$$a_2 = -B\alpha_f^2 \left\{ \frac{(4.0843)(0.3345)}{0.169} + \frac{(1.9537)(0.3244)}{0.131} + \frac{(1.9758)(0.2542)}{0.349} \right\}$$

$$= -1.29 \times 10^{-4} \text{ cm}^{-1}$$

It is seen that the largest term concerns the rotation about the symmetry axis z. Interaction constants a_o, a, and b are related to a_1, a_2, and a_3 as follows

$$a_o + 2a = -a_3$$

$$a_o - a + b = -a_1$$

$$a_o - a - b = -a_2$$

and thus

$$a_o = 0.00177 \text{ cm}^{-1}$$

$$a = 0.00167 \text{ cm}^{-1}$$

$$b = -0.000031 \text{ cm}^{-1}$$

A comparison of these constants with the results of Rayne's experimental analysis of formaldehyde is of interest. The experimental values obtained for formaldehyde are

$$a_o = 0.0165 \text{ cm}^{-1}$$

$$a = 0.0095 \text{ cm}^{-1}$$

$$b = 0.0020 \text{ cm}^{-1}$$

which are larger by a factor of ten than the values calculated for glyoxal. This not surprising since the interaction constants are

directly proportional to the rotational constants A, B, and C which for formaldehyde are approximately (57)

$$C = 8.6 \text{ cm}^{-1}$$

$$A \approx B \approx 1.0 \text{ cm}^{-1}$$

as compared with the glyoxal constants,

$$C = 1.90 \text{ cm}^{-1}$$

$$A \approx B \approx 0.158 \text{ cm}^{-1}$$

The results, therefore, are in agreement at least to the same order of magnitude.

Typical splittings of the symmetric rotor energy levels of glyoxal which are due to the diagonal effect of magnetic interactions are given in Appendix VIII for the evaluated constants α, a_o, and a. Approximate energy level spacings are shown in Figure 6 for several example cases.

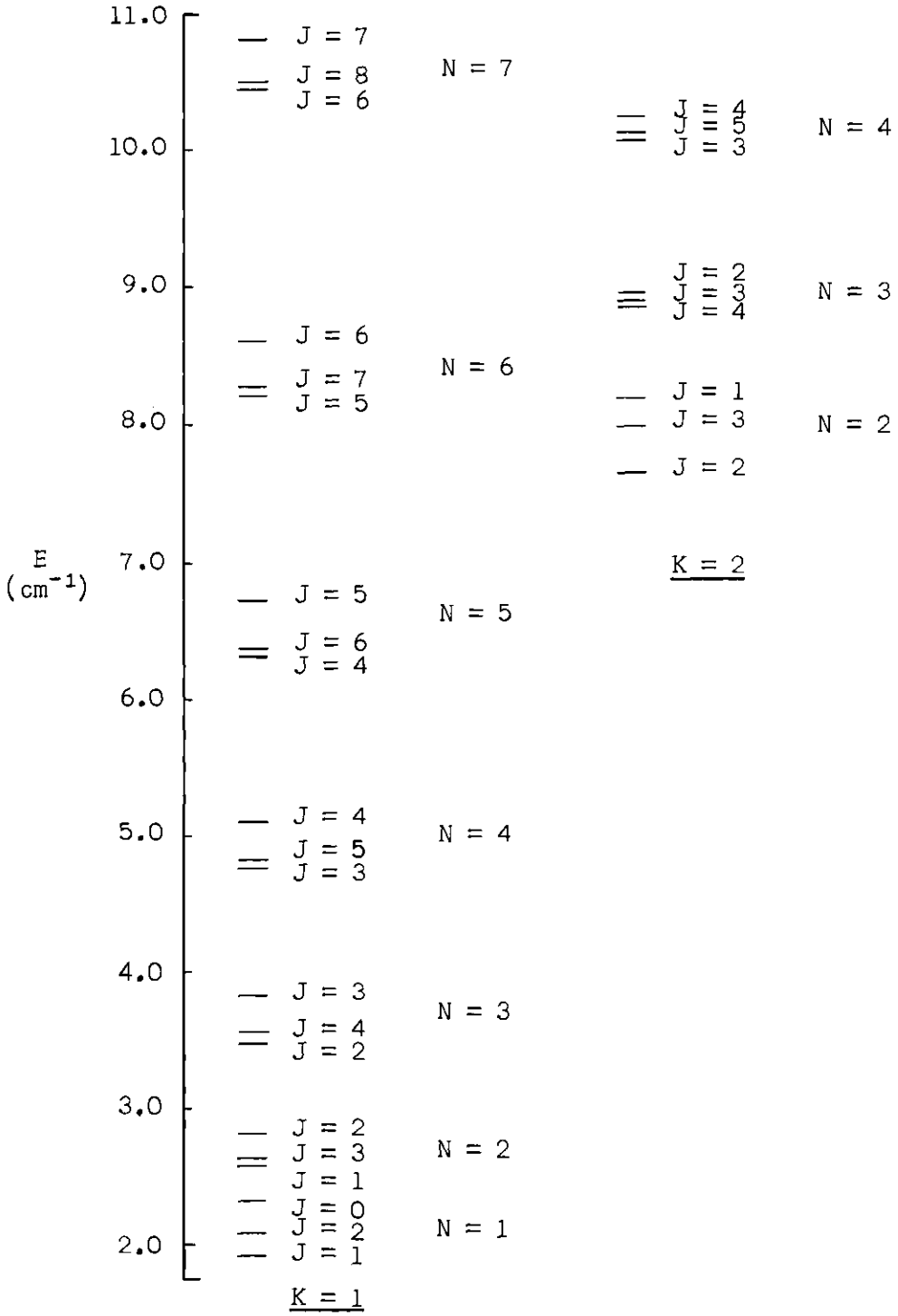


Figure 6. Typical Fine Structure Energy Level Spacings

CHAPTER X

THE TRIPLET STATE OF GLYOXAL IN AN EXTERNAL MAGNETIC FIELD AND THE MAGNETIC ROTATION SPECTRUM

Introduction

A somewhat detailed description of the triplet state energy levels of glyoxal was obtained in Chapter IX using matrix elements of a Hund's case (b) representation which were diagonal in the quantum numbers K and N. In this chapter the treatment is extended to include the effects of an external magnetic field and, subsequently, to discuss the existence of a magnetic rotation spectrum.

Since there is no quantized orbital angular momentum in glyoxal essentially the entire effect of the magnetic field is due to an interaction with electron spin and thus is described by the Hamiltonian

$$H = \mathcal{H}_z \frac{e}{mc} S_z$$

$$= \mathcal{H}_z \frac{e}{mc} \left(\cos(x,Z) S_x + \cos(y,Z) S_y + \cos(z,Z) S_z \right)$$

where $\mathcal{H}_Z$ represents an external magnetic field which is taken as directed along the positive Z axis in a space fixed coordinate system, (X, Y, Z), and S_Z is the total spin angular momentum operator defined relative to the space fixed axis Z. In the latter equality S_Z is related to the spin operators S_x, S_y, and S_z, defined relative to

molecule fixed axes, (x,y,z), by an Eulerian angle transformation involving the cosines of the angles between molecule fixed axes and the space fixed Z axis.

Since relatively weak magnetic fields, i.e., on the order of 2000 gauss, normally are employed in magnetic rotation experiments, it is convenient to adopt the zero field description as a starting point for the analysis. Thus, interactions with the field will be described in terms of zero field solutions characterized by rotational quantum numbers K and N and the three values of the total angular momentum quantum number

$$J = N + 1$$

$$J = N$$

$$N = N - 1$$

For very weak magnetic fields, a simple perturbation of the zero field energy levels provides a satisfactory description, but for increased fields, mixings occur which tend to destroy the significance of individual zero field states. Rigorously of course, only the projection of the total angular momentum on the Z axis, M, is a good quantum number in the presence of a magnetic field and thus a mixing of all states with the same M is allowed.

It is significant that this initial description is exactly the opposite of that expressed by Hameka (58) in a recent theoretical treatment of magnetic rotation spectra. In Hameka's treatment, the triplet state is described by the three components

$$\psi_{+1}\ \psi_{0}\ \psi_{-1}$$

corresponding to the eigenvalues 0 and ± 1 of the spin operator S_Z relative to a space fixed axis. Any tendency of molecular rotation to destroy the individual spin states was ignored, and thus the treatment corresponds to a Paschen Back limit.

In the present work, however, it is assumed that the spin is rather strongly coupled to the molecule by spin-spin, spin-orbit, and spin-rotational interactions, and that any decoupling by the external field must be accompanied by a partial destruction of such interactions. Consequently, this treatment is applicable for weak magnetic fields, but is extendible only with difficulty to the Paschen Back limit.

Energy Levels in an External Magnetic Field

Typical energy level spacings in the absence of external fields are shown in Figure 6 of the previous chapter in which states with different values of J but the same value of N appear closely spaced relative to the separation of states with different N. An exception occurs, however, for small N since the separation of states $N + 1$ and N varies as

$$A(2N + 2)\ cm^{-1} = 0.158(2N + 2)\ cm^{-1}$$

thus, the separation of the $N = 0$ and $N = 1$ levels is only $0.316\ cm^{-1}$.

Energy levels in the case of weak magnetic fields are well described by a first order energy calculation using the zero field wavefunctions. Thus,

$$E = E_o + \frac{e\hbar}{mc} \mathcal{H}_z \langle \psi | S_z | \psi \rangle$$

where $e\hbar/mc = 0.934 \times 10^{-4}$ cm^{-1} gauss^{-1}, H_Z is measured in units of gauss and S_Z in units of $\hbar$, E_o is the zero field energy, and E is the energy in the presence of the magnetic field. Matrix elements of S_Z are easily evaluated for the Hunds' case (b) basis, using the vector model diagram in Figure 7. Projecting S onto J gives

$$S_J = |S| \cos(S,J) = \frac{J(J+1) + S(S+1) - N(N+1)}{2\sqrt{J(J+1)}}$$

and a projection of S_J onto the space fixed Z axis gives the final result,

$$\langle \psi | S_z | \psi \rangle = \frac{M}{2J(J+1)} \left\{ J(J+1) + S(S+1) - N(N+1) \right\}$$

$$= \frac{M}{2J(J+1)} \left\{ J(J+1) - N(N+1) + 2 \right\}$$

where $S = 1$ and M denotes the quantized projection of the total angular momentum on the space fixed Z axis; thus

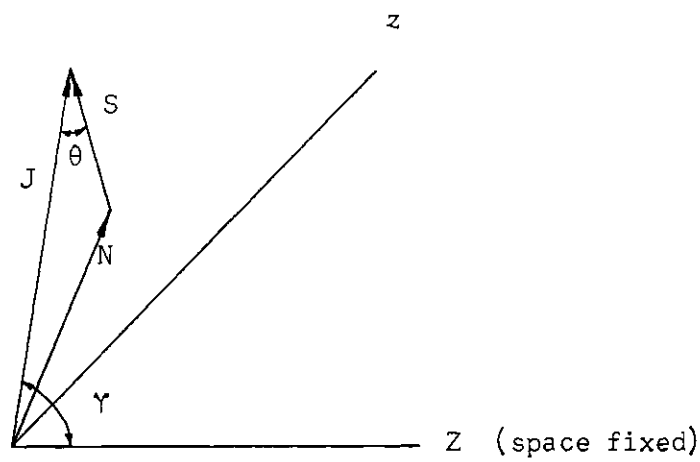
$$M = 0, \pm 1, \pm 2, \cdots, \pm J$$

Simplified expressions for the respective J values are:

$$\langle \psi | S_z | \psi \rangle = \frac{M}{N+1} \qquad J = N+1$$

$$= \frac{M}{N(N+1)} \qquad J = N$$

$$= -\frac{M}{N} \qquad J = N-1$$



$$\text{Cos } \theta = \frac{J(J+1) + S(S+1) - N(N+1)}{2\sqrt{J(J+1)}\ \sqrt{S(S+1)}}$$

$$\text{Cos } \gamma = \frac{M}{\sqrt{J(J+1)}}$$

Figure 7. Vector Model Diagram

Consequently for a fixed N, energy splittings are proportional to M as is the case in the usual weak field Zeeman effect in atoms.

The energy levels thus obtained are shown on Figure 8 for the example case $K = 1$ and $N = 2$. Two features in these results are particularly noteworthy: first, the inverted order of the M components for $J = N + 1$ relative to $J = N - 1$; second, the difference in the number of components for the respective J values.

An extension of the treatment to include a mixing of the zero field states is required in order to describe the effects of an increased magnetic field. Wavefunctions in this case can be constructed as the following sum over all states with the same value of M,

$$\psi = \sum_k c_k \psi_k$$

where the ψ_k are zero field solutions. As a first approximation which is now adequate up to some higher field limit, only mixings between states with different values of J, but the same value of K and N, need be considered; other states corresponding to changes in K and N are more widely separated except in the case of very small N. Neglecting the difficulties for small N, the wavefunction becomes

$$\psi = c_1 \psi_{N+1} + c_2 \psi_N + c_3 \psi_{N-1}$$

where subscripts denote the value of J. Matrix elements of S_Z between the states of different J as given by Hill (59) are given on the following page.

	N+1	N	N-1
N+1	$\frac{M}{N+1}$	$\left\{\frac{N[(N+1)^2 - M^2]}{(N+1)^2(2N+1)}\right\}^{\frac{1}{2}}$	0
N		$\frac{M}{N(N+1)}$	$\left\{\frac{(N+1)(N^2-M^2)}{N^2(2N+1)}\right\}^{\frac{1}{2}}$
N-1			$-\frac{M}{N}$

Corresponding energies obtained by minimizing

$$\langle \psi | H_o + \frac{eh}{mc} \mathcal{H}_z S_z | \psi \rangle$$

where H_o is the zero field Hamiltonian, with respect to the coefficients c_k are shown in Figures 9 and 10 for the example cases $K = 1$, $N = 2$ and $K = 1$, $N = 3$. The zero field splitting is the same as previously obtained in Chapter IX. It is evident that states corresponding to the maximum absolute value of M cannot be mixed with other states, to the extent that mixings with states of different K and N is ignored, and thus these states establish the Paschen Back limit. States with the next largest absolute value of M involve mixings of the $J = N$ and $J = N + 1$ zero field states only, but the other M states involve all three J values. The Paschen Back splitting shown in Figure 9 is

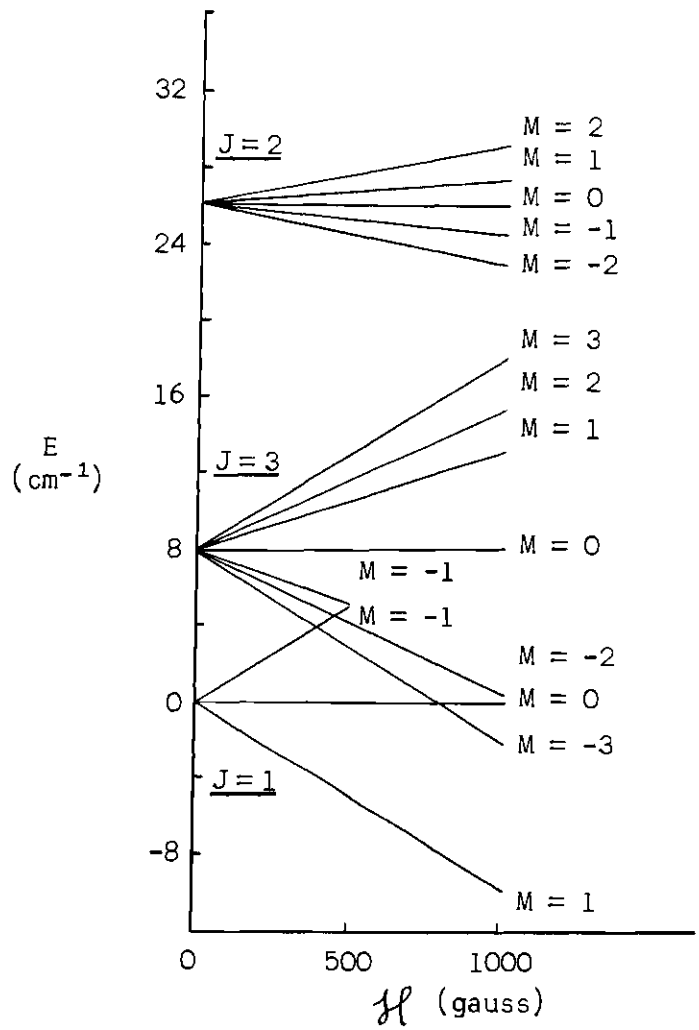


Figure 8. Weak Field Splitting of K = 1, N = 2 Energy Levels

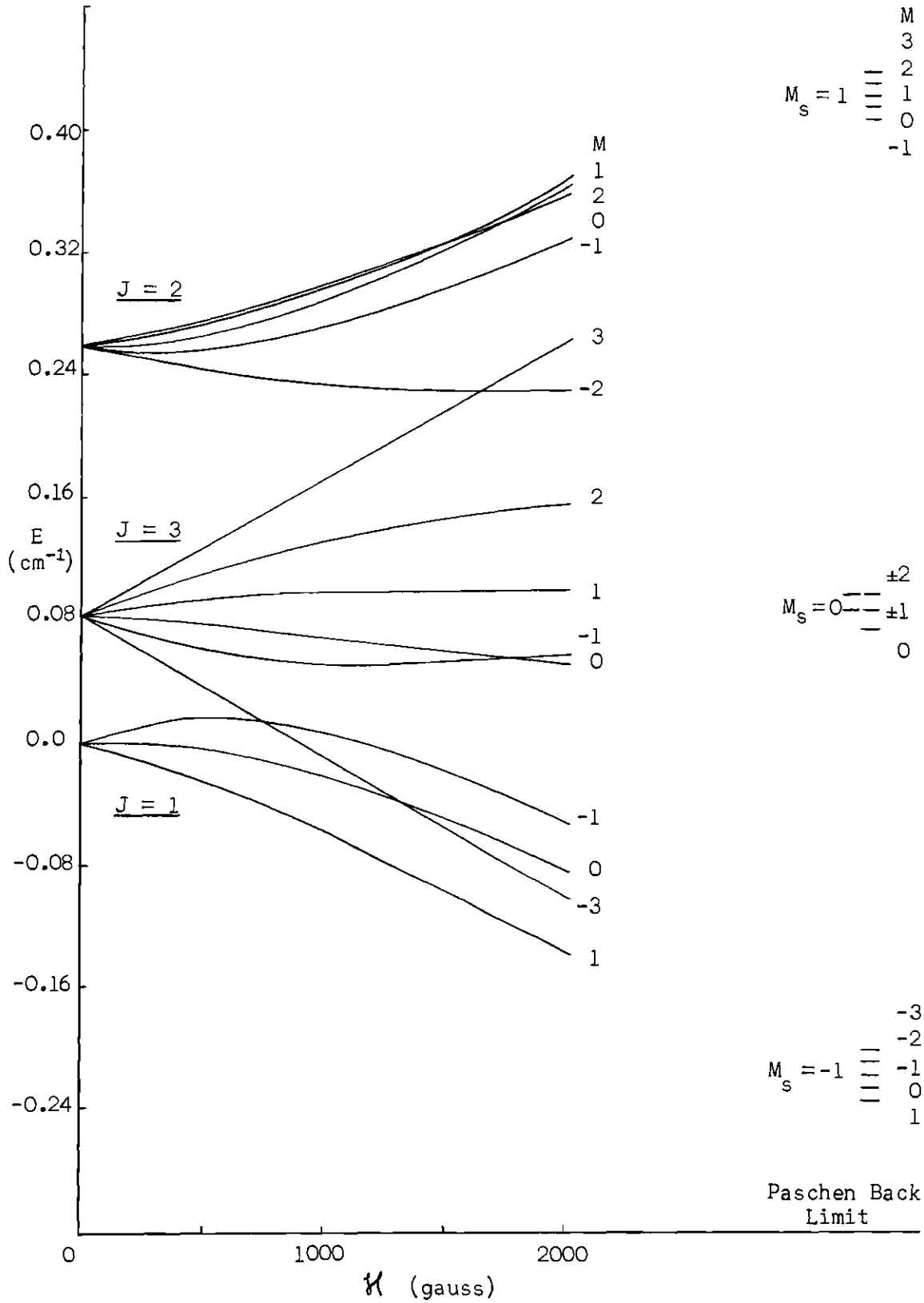


Figure 9. Splitting of K = 1, N = 2 Energy Levels for Increased Magnetic Fields

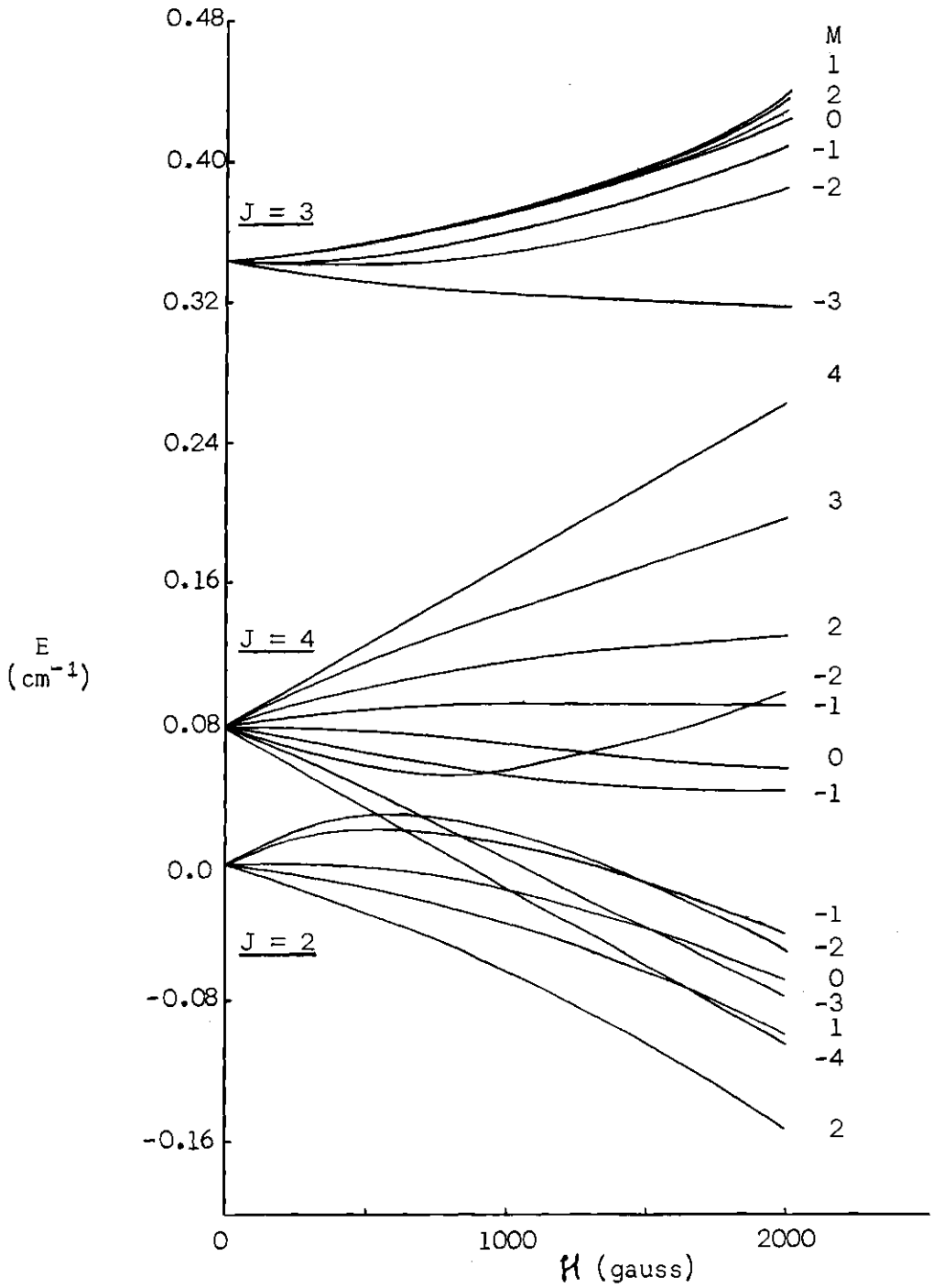


Figure 10. Splitting of K = 1, N = 3 Energy Levels for Increased Magnetic Fields

based on the interaction of electron spin with the rotating molecule assuming no interaction of the rotational magnetic moment with the external field. In the limit of weak fields the splitting resembles that shown in Figure 8, but for fields above 500 gauss, there is considerable deviation from the weak field picture.

Magnetic Rotation Spectra

General Theory

Existing theories of the magnetic rotation phenomenon are reviewed briefly in this section in order to deduce fairly general conclusions which then are used to demonstrate how a magnetic rotation spectrum could arise in the singlet-triplet transition of glyoxal.

In order to understand limitations in the magnetic rotation theory it is necessary to consider certain results from classical radiation theory and to indicate how the classical approach may be modified to agree with the more rigorous quantum theory of radiation. In the simple classical theory the interaction of radiation with a molecule is treated as a time dependent perturbation, using the Hamiltonian H' of Chapter VIII, which has the effect of mixing stationary state wavefunctions, ψ_k, to give the new wavefunction

$$\Psi = c_1(t)\psi_1 + c_2(t)\psi_2 + c_3(t)\psi_3 + \cdots$$

where Ψ provides a description of the molecule during the course of interaction with radiation. The squares of the coefficient magnitudes, $|c_k(t)|^2$, represent the probability of finding the system in a certain

stationary state at a time t. Initially, before interaction with the radiation, the system is assumed to be in a known stationary state, say ψ_1, and thus

$$c_1(0) = 1$$

$$c_k(0) = 0, \quad k > 1$$

The usual time dependent perturbation theory equations, which are given for example by Eyring, Walter, and Kimball (32), or Heitler (43), are then solved for the coefficients $c_k(t)$ as a function of time. In the simplest treatment, the decay of the initial state during the interaction with radiation is ignored, and $c_1(0)$ is kept equal to unity. This assumption is equivalent to the physical statement that the molecule remains in the initial state ψ_1 for a time which is long on the molecular scale. The coefficients which result have the following expression for $k \geq 2$.

$$c_k(t) = \langle \psi_1 | H'' | \psi_k \rangle \left\{ \frac{e^{i(E_k - E_1 + h\nu)\frac{t}{\hbar}} - 1}{E_k - E_1 + h\nu} + \frac{e^{i(E_k - E_1 - h\nu)\frac{t}{\hbar}} - 1}{E_k - E_1 - h\nu} \right\}$$

where the ψ_k are the time independent wavefunctions of Chapter VIII, ν is the frequency of the incident radiation, E_k is the stationary state energy of the k^{th} molecular state, and H'' is the spatial part of the Hamiltonian, H'.

The treatment just indicated is quite satisfactory for a discussion of transition probabilities, but it has the disadvantage of giving an undefined wavefunction at the resonant frequency,

$\nu = (E_k - E_1)/h$. The reason for the failure at resonance is due to the neglect of the decay of the initial state with time, i.e., the assumption that $c_1(t) = 1$. In order to take this variation in $c_1(t)$ into account, Weisskopf and Wigner (60) have extended the theory by introducing a damping constant Γ which describes the decay of the initial state as the exponential

$$c_1(t) = e^{-\Gamma t}$$

and as a consequence the denominators of the $c_k(t)$ expressions become,

$$E_k - E_1 + h\nu + i\Gamma$$

The introduction of a damping constant in this manner brings the classical treatment into agreement with quantum theory formulation of Heitler and Ma (61).

There are at least two ways to apply the results of general radiation theory to a description of magnetic rotation. In one approach (62) the effect of radiation on the medium is described by determining time dependent molecular wavefunctions,

$$\Psi = c_1(t)\Psi_1 + c_2(t)\Psi_2 + \cdots$$

and using the wavefunction to compute average electric and magnetic moments m and μ for individual molecules. Individual molecular moments then are used to compute a macroscopic electric displacement, D, and magnetic induction, B,

$$D = E + 4\pi N m$$

$$B = \mathcal{H} + 4\pi N \mu$$

where E and $\mathcal{H}$ are the electric and magnetic field strengths which characterize the radiation field, and N is the number of molecules per unit volume. If the propagation of radiation through the medium is required to satisfy Maxwell's equations connecting D and B, then only two allowed indices of refraction result, one of which corresponds to the index of refraction of right circularly polarized radiation, n_+, and the other to left circularly polarized radiation, n_-. The angle through which the beam of polarized radiation is rotated then can be expressed as proportional to the difference of indices of refraction,

$$\Theta = \frac{\pi l \nu}{c}(n_- - n_+)$$

The following explicit formula was derived by Kramers (63) and applied by Serber (64) in a treatment of the Faraday effect,*

$$\frac{\Theta}{l} = \frac{4\pi^2 \nu^2 N i}{ch} \sum_{nn'} \frac{\{\langle n|x|n'\rangle\langle n'|y|n\rangle - \langle n|y|n'\rangle\langle n'|x|n\rangle\}}{\nu^2 - \nu_{n'n}^2} \frac{e^{-E_n/kT}}{Q}$$

$$= -\frac{8\pi^2 \nu^2 N}{ch} \sum_{nn'} \mathrm{Im}\left(\frac{\langle n|x|n'\rangle\langle n'|y|n\rangle}{\nu^2 - \nu_{n'n}^2}\right) \frac{e^{-E_n/kT}}{Q}$$

---

*The Faraday effect refers to a magnetic rotation phenomenon in which the frequency of the incident radiation is far removed from any absorption frequency of the sample.

where ℓ is the length of the sample, n' and n are excited and ground states, respectively, E_n is the energy of the ground state, Q is the classical partition function, and $\nu_{n'n} = (E_{n'} - E_n)/h$. The ground and excited state energy levels, E_n and $E_{n'}$, are those in the presence of the external magnetic field.

The formula may be rewritten as follows to show an explicit dependence on the absorption of right and left circularly polarized radiation.

$$\frac{\Theta}{\ell} = -\frac{2\pi^2 N e^2 \nu^2}{hc} \sum_{n'n} \left\{ \frac{|\langle n'|x-iy|n\rangle|^2 - |\langle n'|x+iy|n\rangle|^2}{\nu^2 - \nu_{n'n}} \right\} e^{-E_n/kT}$$

If the transition $n' \leftarrow n$ corresponds to an absorption of left circularly polarized radiation, then

$$\langle n'|x+iy|n\rangle$$

is nonvanishing, and similarly

$$\langle n'|x-iy|n\rangle$$

is nonvanishing in case right circularly polarized radiation is absorbed.

A second theoretical description of the magnetic rotation phenomena has been formulated by Hameka (58) based on the damping theory of Heitler and Ma (61). The treatment involves an introduction of damping constants, as in the Weisskopf and Wigner theory (60), for every possible transition between molecular states; but, in order to gain tractability, Hameka has limited the consideration to transitions between

ground and excited states, and has neglected transitions between components of the excited state.* An expression, $|b_{o,\lambda\mu}|^2$, was obtained for the probability of absorption of photon with wavelength λ polarized in the x direction, and simultaneous emission of a photon with wavelength μ polarized in the y direction. In the expression given below, Hameka's result is rewritten with only a slight loss of generality to conform to the classical rather than purely quantum mechanical theory of radiation. In addition, only the electric dipole term in the expansion of the vector potential of the radiation field is considered.

$$b_{o,\lambda\mu} = \frac{1}{-\frac{hc}{\lambda} + \frac{hc}{\mu} + \frac{1}{2}ih\Gamma} \sum \frac{\langle n|y|n'\rangle\langle n'|x|n\rangle}{h\nu - (E_{n'} - E_n) + \frac{1}{2}ih\gamma_{n'}}$$

where x and y represent the electric dipole operators for the interaction with the radiation field, Γ and $\gamma_{n'}$, are damping constants for the ground and excited states, respectively, E_n and $E_{n'}$, are ground and excited state energies, and ν is the frequency of the incident radiation.

It is significant to note that the expression for $b_{o,\lambda\mu}$ is of exactly the same form as the well-known Kramers-Heisenberg dispersion formula (65), and differs only in the inclusion of damping constants. Presumably, this implies that a rederivation of the Kramers-Heisenberg

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*In order to justify this assumption, it is necessary to assume that the separation of the components of the excited state is significantly greater than the half-width of emission lines corresponding to transitions from the respective components.

formula using the Weisskopf-Wigner damping theory would lead to a result equivalent to Hameka's.

Finally, it is of interest to show that the above formulation exhibits the essential features of Serber's theory. Thus, consider the identities,

$$\langle n|y|n'\rangle\langle n'|x|n\rangle = \langle n|y|n'\rangle\langle n'|x+iy|n\rangle - i\langle n|y|n'\rangle\langle n'|y|n\rangle$$

in which the first term on the right vanishes in case $\Delta m = -1$, and

$$\langle n|y|n'\rangle\langle n'|x|n\rangle = \langle n|y|n'\rangle\langle n'|x-iy|n\rangle + i\langle n|y|n'\rangle\langle n'|y|n'\rangle$$

in which the first term on the right vanishes in case $\Delta m = +1$. Separation of the summation over all states into $\Delta m = +1$ transitions and $\Delta m = -1$ transitions gives

$$b_{0,\lambda\mu} = \frac{i}{\frac{hc}{\mu} - \frac{hc}{\lambda} + i\frac{\hbar}{2}\Gamma}\left\{ \sum_{nn'}^{\Delta m=+1} |\langle n|y|n'\rangle|^2 \left[h\nu - (E_{n'}-E_n) + i\frac{\hbar}{2}\gamma_{n'}\right]^{-1} - \sum_{nn'}^{\Delta m=-1} |\langle n|y|n'\rangle|^2 \left[h\nu - (E_{n'}-E_n) + i\frac{\hbar}{2}\gamma_{n'}\right]^{-1}\right\}$$

The Kramers formula, which is Serber's starting point, also may be rewritten using the same technique to give

$$\frac{\Theta}{\ell} = \frac{8\pi^2\nu^2 N}{ch}\left\{ \sum_{nn'}^{\Delta m=-1} |\langle n|y|n'\rangle|^2 (\nu^2 - \nu_{n'n}^2)^{-1} \frac{e^{-E_n/kT}}{Q} - \sum_{nn'}^{\Delta m=+1} |\langle n|y|n'\rangle|^2 (\nu^2 - \nu_{n'n}^2)^{-1} \frac{e^{-E_n/kT}}{Q}\right\}$$

Therefore, the conclusion of both theories is that magnetic rotation in a given region of the spectrum is due to a difference in interaction of right and left circularly polarized radiation with the sample, or equivalently, is due to a difference in intensities of the $\Delta m = -1$ and $\Delta m = +1$ transitions.

Magnetic Rotation in a Singlet-Triplet Transition

The discussion of magnetic rotation is concluded in this section by giving a concrete example of the phenomenon in the singlet-triplet transition of glyoxal. Only a simple treatment is presented based on general theoretical conclusions of the previous section and the splitting of excited state energy levels in the presence of a magnetic field. The question of relative intensities of transitions is not considered. However, despite the simplicity of the treatment, the essential features of the magnetic rotation phenomenon are clearly illustrated.

Since the direction of observation in magnetic rotation experiments is colinear with the axis of the magnetic field, only transitions corresponding to $\Delta M = \pm 1$ are observed. The important conclusion of both theoretical descriptions is that rotation of the beam of polarized radiation, or alternatively, the intensity of transmitted radiation polarized perpendicular to the incident radiation, is due to a difference in interaction of the sample with right and left circularly polarized components of the radiation. That is, the phenomenon is attributed to a difference in probabilities of $\Delta M = +1$ and $\Delta M = -1$ transitions. If an excited state can be reached by both $\Delta M = +1$ and $\Delta M = -1$

transitions, at the same frequency, then such transitions tend to cancel in rotational effects. In order to determine the extent of cancellation, it is necessary to consider in detail the relative intensities of the transitions which depend on the magnitude of the dipole moment matrix elements. Useful qualitative information can be obtained, however, by listing the possible transitions to individual M components of the excited state.

As an example, consider the excited states of glyoxal characterized by the rotational quantum numbers $K = 1$ and $N = 2$, and corresponding values of M. Energy levels are shown in Figure 11 as a function of magnetic field strength. Transitions to the excited state of the following types can occur.

$$\Delta N = +2 \quad (N' = 2 \leftarrow N'' = 0)$$
$$\Delta N = +1 \quad (N' = 2 \leftarrow N'' = 1)$$
$$\Delta N = 0 \quad (N' = 2 \leftarrow N'' = 2)$$
$$\Delta N = -1 \quad (N' = 2 \leftarrow N'' = 3)$$
$$\Delta N = -2 \quad (N' = 2 \leftarrow N'' = 4)$$

The value of J'' for the ground state is necessarily the same as N'', and thus the possible values of M'' are:

$$M'' = 0, \pm 1, \pm 2, \ldots, \pm N''$$

In the figure, allowed transitions to individual M' sublevels are listed using the notation + if a transition corresponds to $\Delta M = +1$

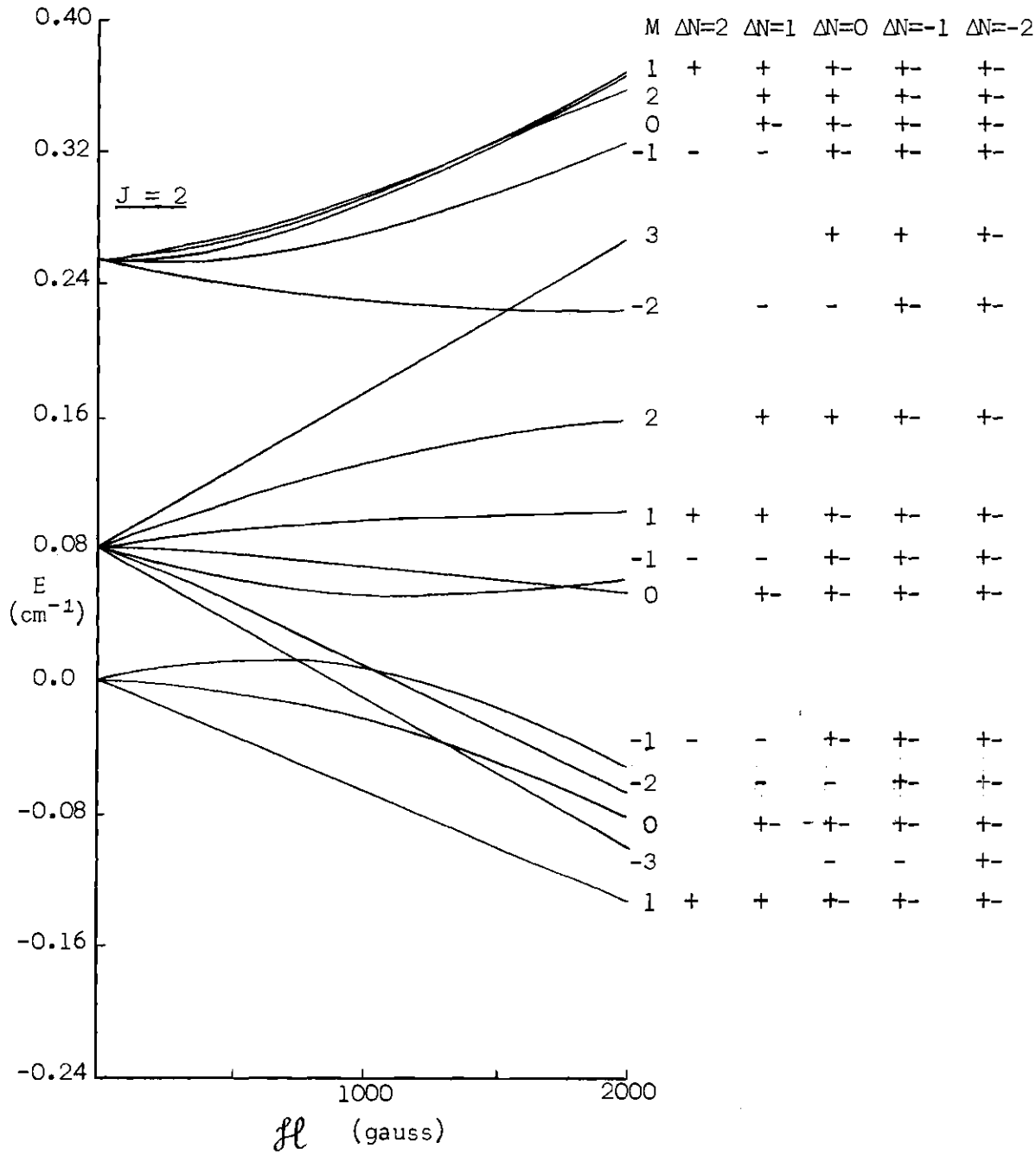

Figure 11. Allowed Transitions to Sublevels of the Excited State K = 1, N = 2

and a - for $\Delta M = -1$. Transitions with $\Delta M = 0$ are not shown. It is seen that in certain regions of the energy spectrum transitions of the type $\Delta M = +1$ predominate and, in other regions, the transitions correspond to $\Delta M = -1$. Therefore, on the basis of the general theory, such regions should exhibit rotational effects, whereas in the regions corresponding to both $\Delta M = +1$ and -1 a partial cancellation of effects occurs.

CHAPTER XI

SUMMARY OF THE GLYOXAL CALCULATIONS

In order to obtain a fairly detailed description of the triplet state energy levels of glyoxal, calculations were performed to determine splittings of the symmetric rotor energy levels caused by magnetic interactions involving electron spin. The description was based on Van Vleck's treatment of the coupling of angular momenta in molecules and as such involved the derivation of an effective Hamiltonian which expressed the combined effects of spin-spin, spin-orbit, and spin-rotational interactions. Explicit formulas for interaction constants in this Hamiltonian were derived in terms of integrals over electronic wavefunctions.

Simple molecular orbital wavefunctions for the ground and excited states of glyoxal were constructed from general principles as linear combinations of atomic orbitals. Spin-spin and spin-orbit interaction integrals were evaluated subsequently by replacing atomic orbitals by the Gaussian function expansions discussed in Part I of the thesis. This application of Gaussian functions proved to be of considerable utility since certain of the multicenter integrals are extremely difficult to evaluate using hydrogen-like orbitals. Evaluations also were accomplished with much less difficulty than would be the case if conventional Gaussian function expansions involving angular variables θ and φ were used.

Final expressions for energy levels were obtained using the matrix elements of the effective Hamiltonian which were diagonal in the rotational quantum numbers K and N for a Hunds' case (b) representation. The splitting of states with different values of J, but the same values of K and N, was shown to be primarily due to spin-spin interactions.

The probability of transition from the ground state of glyoxal, ^1A_g, to the excited triplet state, ^3A_u, was calculated on the basis of a detailed consideration of the mixing of singlet and triplet wavefunctions caused by spin-orbit interaction. In addition, the probability of transition to the singlet state, ^1B_g, by a magnetic dipole mechanism was determined. The oscillator strengths for the $^3A_u \leftarrow {}^1A_g$ and $^1B_g \leftarrow {}^1A_g$ transitions were determined to be approximately 0.8×10^{-7} and 5×10^{-7}, respectively. In both calculations, Gaussian function expansions were used to evaluate integrals over electronic wavefunctions.

Energy levels of glyoxal in the presence of an external magnetic field were determined in general for weak magnetic fields and for several example cases for increased fields. In the latter case, mixing of states of different J, but the same value of K and N, was considered. The results indicated considerable deviations from the weak field picture for fields greater than about 1000 gauss.

A connection between two different theories of the magnetic rotation phenomenon was established based on the difference in probabilities of $\Delta M = +1$ and -1 transitions. The general nature of a magnetic rotation spectrum was indicated for several example transitions.

A P P E N D I C E S

APPENDIX I

HYDROGEN MOLECULE AND MOLECULE ION INTEGRALS

Hydrogen Molecule Ion

The three-center treatments of H_2^+ given in Chapter I require evaluation of certain overlap, kinetic energy, and nuclear potential integrals between exponential functions centered at the nuclei and either an exponential or Gaussian function centered midway between the nuclei. Integrals involving only exponential functions with equal scale factors are well known and are given for example by Rosen (52). Those involving the Gaussian center function were derived in the course of this work by transformation to elliptical coordinates. Final integral formulas are given in terms of the notation,

$$S_A = a^{3/2}\pi^{-1/2}\exp(-ar_A)$$

$$S_B = (2b/\pi)^{3/4}\exp(-br_B^2)$$

$$S_C = a^{3/2}\pi^{-1/2}\exp(-ar_A)$$

where A and C denote nuclei separated by a distance 2R, and B denotes the point midway between the nuclei. In addition,

$$N = (2a^2/b)^{3/4}\pi^{-1/4}\exp(a^2/4b) \qquad E = \exp(-aR)$$

$$G_1 = \int_{-b^{1/2}R + a/2b^{1/2}}^{b^{1/2}R + a/2b^{1/2}} \exp(-u^2)\,du \qquad G_2 = \int_{b^{1/2}R + a/2b^{1/2}}^{\infty} \exp(-u^2)\,du$$

$$G_3 = \int_{-b^{1/2}R + a/2b^{1/2}}^{\infty} \exp(-u^2)\,du \qquad G_4 = \int_{-(2b)^{1/2}R}^{(2b)^{1/2}R} \exp(-u^2)\,du$$

Final formulas are:

$$\langle S_A | S_B \rangle = N\left\{ (1 - (a/2bR))\, E\, G_3 + (1 + (a/2bR))(G_2/E) \right\}$$

$$\langle S_A | -\tfrac{1}{r_A} | S_B \rangle = -\frac{N}{R}\left\{ E\, G_3 - (G_2/E) \right\}$$

$$\langle S_A | -\tfrac{1}{r_C} | S_B \rangle = -\frac{N}{R}\left\{ E G_1 - E G_2 + (G_2/E) - 2a\, G_1 G_2\, b^{-1/2} \exp\left(a^2/4b + bR^2\right) \right\}$$

$$\langle S_B | -\tfrac{1}{r_A} | S_B \rangle = -(\pi R^2)^{-1/2}\, G_4$$

$$\langle S_B | -\tfrac{1}{2}\nabla^2 | S_B \rangle = 3/2\, b$$

$$\langle S_A | -\tfrac{1}{2}\nabla^2 | S_B \rangle = -\frac{a^2}{2}\langle S_A | S_B \rangle - a \langle S_A | -\tfrac{1}{r_A} | S_B \rangle$$

$$\langle S_A | S_C \rangle = E^2 \left(1 + 2aR + (2aR)^2/3\right)$$

$$\langle S_A | -\tfrac{1}{2}\nabla^2 | S_A \rangle = \tfrac{1}{2} a^2$$

$$\langle S_A | -\tfrac{1}{r_A} | S_A \rangle = -a$$

$$\langle S_A | -\tfrac{1}{2}\nabla^2 | S_c \rangle = a^2 E^2 \left(\tfrac{1}{2} + aR - (2aR)^2/6 \right)$$

$$\langle S_A | -\tfrac{1}{r_c} | S_A \rangle = a \left\{ -\frac{1}{2aR} + E^4 \left(1 + \frac{1}{2aR} \right) \right\}$$

$$\langle S_A | -\tfrac{1}{r_c} | S_c \rangle = -aE \left(1 + 2aR \right)$$

One additional integral is required in case the center function is an exponential (53), $S_B^e = a^{3/2} \pi^{-1/2} \exp(-a r_B)$

$$\langle S_A | -\tfrac{1}{r_c} | S_B^e \rangle = -a \left\{ -12 D/R + \left(3aR + 9 + 9/aR \right) E - \left(9/aR + 2 \right) E^3 \right\}$$

$$D = \left\{ \left((aR)^2/3 + aR + 1 \right) \left(\log_e 2 + E_1(-2aR) \right) E - \left((aR)^2/3 - aR + 1 \right) \left(E_1(-4aR) \right) E^{-1} \right\}$$

$$E_1(x) = -\int_x^\infty \frac{1}{u} \exp(-u)\, du$$

Formulas for all other integrals involving s_B^e are obtainable from the s_A and s_C expressions by replacing 2aR by aR.

Hydrogen Molecule

The one electron integrals that occur in H_2 are the same as those previously obtained in the exponential three-center treatment of H_2^+. Formulas for electron repulsion integrals involving exponential functions on one and two centers are readily available, but the four three-center integrals required are evaluated only with difficulty. Expressions for two of the three-center integrals and numerical values at several internuclear distances for the other two are given by Hirschfelder (54), however, in connection with a treatment of H_3.

Final formulas written in a computer program form are given on the following pages. Certain notational changes have been made.

R (program)	=	aR	F2	=	$E_1(-2aR)$
C	=	a	F4	=	$E_1(-4aR)$
B	=	2aR	F8	=	$E_1(-8aR)$
EFR	=	$E_1(-4aR)$	ov	=	$\langle S_A \mid S_C \rangle$
ETR	=	$E_1(-2aR)$	u	=	E
EE	=	E^2	L	=	3.0

and

$$\text{ABAC} = \left\langle \phi_A(1)\,\phi_B(2) \mid \frac{1}{r_{12}} \mid \phi_A(1)\,\phi_C(2) \right\rangle, \text{ etc.}$$

```
2       ABAB  = (C/R)(1.0-((1.0+(1.375.R)+(0.75.R.R)+(R.R.R/6.0)
2       )(U.U)))                                                    $


2       AAAB = (U.C)( R+0.125+(5.0/(16.0.R))+ ((-0.125-(5.0/(16.0.R)))(
2       U.U)))                                                      $


2       AABB=(-0.2.C.U.U.(-3.125 +(5.75.R)+(3.0.R.R)+((R.R.R)/3.0)) +
2      (((1.2.C)/R)(((OV.OV)(0.5772157+LOG(R))) +((EFR/(U.U))(1.0-R+(R.
2       R/3.0))(1.0-R+(R.R/3.0))) - (2.0.OV.ETR.(1.0-R+(R.R/3.0))/U)))$


2       TABC=(1.0/81.0)(((EE.E/16.0)((131.0/(3.0.R))+1670.0+(2256.0.R)+
2       (624.0.R.R)))- ((EE.EE.E/16.0)((131.0/(3.0.R))+34.0 +(160.0.R).
2       )-(((116.0/(9.0.R))+(116.0/3.0) + (44.0.R) + (16.0.R.R))(F2 + (
2       2.0.LOG(2.0)))(EE.E)) + ((1.0/(EE.E))(F8)((116.0/(9.0.R))-(116.
2       0/3.0) + (44.0.R) - (16.0.R.R))))                           $
```

```
2       D=((E)((R.R/3.0)+R+1.0)(LOG((L+1.0)/(L-1.0)) + F2))  - ((1.0/E)
2       ((R.R/3.0)-R+1.0)(F4))                                          $

2       K0= (0.25/R)(((3.0)((L.L)+1.0)(D)) - (6.0.L.E.((R.R/3.0)+R+1.0)
2       ) +(((6.0.L)-(2.0.R))(EE.E)))                                   $

2       K2=(0.75/R)((D-(3.0.D.L.L))   + (6.0.L.E.((R.R/3.0)+R+1.0)) - (
2       ((6.0.L)+(2.0.R))(EE.E)))                                       $

2       ABAC = K0 + K2 -TABC                                            $

2       D = (((B.B/3.0) + B + 1.0).E.(LOG(2.0.B) +   0.5772157  )) -
```

```
2        (((B.B/3.0)-B + 1.0).F4/E)                                          $


2        TBAC=(1.0/105.0)(((16.0.R.R.R.R)(7.0 + (2.0.R.R))(F2-(2.0.F4)))
2        + (EE.((16.0.R.R.R.R.R) - (8.0.R.R.R.R) + (64.0.R.R.R) - (40.0.
2        R.R)+(52.0.R) + 108.0 - (51.0/R)))+ (EE.EE.((4.0.R.R.R.R) - (16
2        .0.R.R.R.R.R) - (58.0.R.R.R) + (15.5.R.R) - (8.5.R) + 33.375 +
2        (51.0/R))))                                                         $


2        K0= (0.25/B)(((3.0)(2.0)(D)) - (6.0.E.((B.B/3.0)+B+1.0)
2        ) +(((6.0) - (2.0.B)).E))                                           $


2        BABC = K0 - TBAC                                                    $
```

Numerical values for the two integrals, AACB and ACBB, for which formulas are not available, were obtained by the following interpolation method based on the exact value given in Hirschfelder's H_3 calculation and the Mulliken approximation.

$$AACB_R = AACB_R^M - AACB_{R_o}^M + AACB_{R_o}^{Exact}$$

where, the subscript denotes the internuclear distance, and M implies evaluation by the Mulliken approximation. The exact value of the integral is assumed known at R_o.

Three-center integrals obtained by Hirschfelder (54) and also calculated using the four-term 1s approximation of Chapter II are given in Table 10.

Table 10. Three-Center Electron Repulsion Integrals

R (a.u.)	ABCB		ACAB	
	Gaussian Approximation	Hirschfelder	Gaussian Approximation	Hirschfelder
0	0.6253947	0.625000	0.6253947	0.625000
0.5	0.5224915	-	0.5570509	-
1.0	0.3362046	0.335838	0.4178326	0.417063†
1.5	0.1861568	0.186210	0.2865386	0.286059
2.0	0.0928459	0.094214	0.1884586	0.188392
2.5	0.0418684	0.044874	0.1216000	0.1219667
3.0	0.0170727	0.02491	0.0776739	0.0784356
4.0	0.00209788	0.0039228	0.03077694	0.032225
6.0	0.00000753	0.000117844	0.00396597	0.0053549

†The value 0.417424 was obtained using formulas given by Hirschfelder instead of the value reported in the table.

Table 10 - Continued

R (a.u.)	AACB		ACBB	
	Gaussian Approximation	Hirschfelder	Gaussian Approximation	Hirschfelder
0	0.6253947	0.625000	0.6253947	0.625000
0.5	0.4949080	-	0.5514621	-
1.0	0.2769390	0.278796	0.3962716	0.399463
1.5	0.1259661	0.217762	0.2482045	0.247086
2.0	0.0494084	0.051214	0.1417734	0.141207
2.5	0.0168378	0.0187244	0.0758985	0.075091
3.0	0.00499573	0.00641576	0.0385729	0.039101
4.0	0.00029281	0.00065391	0.0085508	0.009128
6.0	0.00000016	0.0000047688	0.00021721	0.00043635

APPENDIX II

DERIVATION OF GAUSSIAN FUNCTION INTEGRALS

The derivations of the Gaussian function integral formulas of Chapter III are outlined in this appendix. Those involving overlap, kinetic energy, nuclear potential, and electron repulsion operators were obtained by Boys (15), and are included here for completeness.

There is one unique mathematical property of the Gaussian function that requires special mention since it is the essential reason for simplicity of the integrals. Consider the two normalized Gaussian functions,

$$\varphi_A = (2a/\pi)^{3/4} \exp(-a r_A^2)$$

$$\varphi_B = (2b/\pi)^{3/4} \exp(-b r_B^2)$$

where A and B are points in space with coordinates (A_x, A_y, A_z) and (B_x, B_y, B_z), respectively, using the notation of Chapter III. The product of φ_A and φ_B, using the law of cosines, is

$$\varphi_A \varphi_B = (2/\pi)^{3/2} (ab)^{3/4} \exp(-a r_A^2 - b r_B^2)$$

$$= (2/\pi)^{3/2} (ab)^{3/2} \exp\left(-\frac{AB^2 ab}{a+b}\right) \exp\left(-(a+b) r_P^2\right)$$

where

$$r_P^2 = (x - P_x)^2 + (y - P_y)^2 + (z - P_z)^2$$

$$AB^2 = (A_x - B_x)^2 + (A_y - B_y)^2 + (A_z - B_z)^2$$

and

$$P_x = \frac{aA_x + bB_x}{a+b} \qquad P_y = \frac{aA_y + bB_y}{a+b} \qquad P_z = \frac{aA_z + bB_z}{a+b}$$

The important result thus obtained is that a product of two Gaussian functions is once again a Gaussian function, but relative to a new origin.

Overlap

The integral $\langle \varphi_A | \varphi_B \rangle$ is easily obtained by direct integration, after defining the product origin P.

$$\langle \phi_A | \phi_B \rangle = \left(\frac{2}{a+b}\right)^{3/2} (ab)^{3/4} \exp\left(-AB^2 ab/(a+b)\right)$$

Kinetic Energy

The kinetic energy operator, $-\frac{1}{2}\nabla^2$, is conveniently translated to an origin at B before differentiation. Subsequent integration gives the result

$$\langle \phi_A | -\tfrac{1}{2}\nabla^2 | \phi_B \rangle = \langle \phi_A | \phi_B \rangle \left\{ \frac{3ab}{a+b} - \frac{2AB^2 a^2 b^2}{(a+b)^2} \right\}$$

Nuclear Attraction

It is convenient first to evaluate,

$$\int \frac{1}{r_{12}} \exp(-a r_{2A}^2)\, dv_2$$

by expansion of the Coulomb potential of the spherical charge distribution, $\exp(-ar_{2A}^2)$.

$$\int \frac{1}{r_{12}} \exp(-ar_{2A}^2)\, dv_2 = \frac{4\pi}{r_{1A}} \int_0^{r_{1A}} r_{2A}^2 \exp(-ar_{2A}^2)\, dv_2 + 4\pi \int_{r_{1A}}^{\infty} r_{2A} \exp(-ar_{2A}^2)\, dv_2$$

$$= (2\pi/ar_{1A}) \int_0^{r_{1A}} \exp(-ar_{2A}^2)\, dv_2$$

where point 1 is considered fixed in space. Identification of the origin of the potential $\frac{1}{r_E}$ in the nuclear attraction integral, $\langle \phi_A | -\frac{1}{r_E} | \phi_B \rangle$, with the point 1 gives the result obtained by Boys

$$\langle \phi_A | -\frac{1}{r_E} | \phi_B \rangle = -2 \left(\frac{a+b}{\pi}\right)^{1/2} \langle \phi_A | \phi_B \rangle F(EP^2(a+b))$$

where $F(z) = z^{-1/2} \int_0^{z^{1/2}} \exp(-u^2)\, du$, $EP^2 = \sum_{k=x,y,z} \left(E_k - \frac{aA_k + bB_k}{a+b}\right)$

Electron Repulsion

The evaluation of $(\phi_A(1)\phi_B(1) | \frac{1}{r_{12}} | \phi_C(2)\phi_D(2))$ follows the previous derivation except an additional integration over the coordinates of electron 1 must be performed. Thus the integral

$$\frac{2\pi}{v} \int \exp(-ur_{1P}^2)\, \frac{1}{r_{1Q}} \int_0^{r_{1Q}} \exp(-v\omega^2)\, d\omega\, dv_1$$

is obtained, where $v = c + d$ and $u = a + b$. The final formula obtained by Boys is given in Chapter III.

Spin-orbit Interaction

An evaluation of the following three basic integrals given in Chapter VIII is required,

$$h_x = \int \frac{1}{r_E}\left(\frac{\partial \phi_A}{\partial z}\frac{\partial \phi_B}{\partial y} - \frac{\partial \phi_A}{\partial y}\frac{\partial \phi_B}{\partial z}\right) dv$$

$$h_y = \int \frac{1}{r_E}\left(\frac{\partial \phi_A}{\partial x}\frac{\partial \phi_B}{\partial z} - \frac{\partial \phi_A}{\partial z}\frac{\partial \phi_B}{\partial x}\right) dv$$

$$h_z = \int \frac{1}{r_E}\left(\frac{\partial \phi_A}{\partial y}\frac{\partial \phi_B}{\partial x} - \frac{\partial \phi_A}{\partial x}\frac{\partial \phi_B}{\partial y}\right) dv$$

where the potential function has origin at (E_x, E_y, E_z) and the Gaussian functions have origins at (A_x, A_y, A_z) and (B_x, B_y, B_z).

Differentiation of ϕ_A and ϕ_B in the h_z integral gives

$$\frac{1}{r_E}\left(\frac{\partial \phi_A}{\partial y}\frac{\partial \phi_B}{\partial x} - \frac{\partial \phi_A}{\partial x}\frac{\partial \phi_B}{\partial y}\right)$$

$$= 4ab\left(4ab/\pi\right)^{3/4}\left\{(A_x - B_x)\left(\frac{y}{r_E}\right) + (B_y - A_y)\left(\frac{x}{r_E}\right) + A_y B_x - B_y A_x\right\} e^{-ar_A^2 - br_B^2}$$

Integrals containing y/r_E or x/r_E times a product of Gaussian functions may be derived from the basic integral,

$$\int \frac{1}{r_E} e^{-ar_A^2 - br_B^2} dV_1$$

by differentiation with respect to parameters $P_x = \frac{aA_x + bB_x}{a+b}$ etc. Mathematical conditions are sufficient for this differentiation.

$$\int \frac{1}{r_E} e^{-ar_A^2 - br_B^2} dv = \exp\left(-AB^2 \frac{ab}{a+b}\right) \int \frac{1}{r_E} e^{-(a+b)r_P^2} dv$$

$$= \frac{2\pi}{a+b} \exp\left(-AB^2 \frac{ab}{a+b}\right) F\left(EP^2(a+b)\right)$$

where

$$F(z) = z^{-1/2} \int_0^{z^{1/2}} \exp(-u^2)\, du$$

Differentiation with respect to P_x gives

$$\int \frac{(x - P_x)}{r_E} e^{-(a+b)r_P^2} dv = \frac{2\pi}{a+b} \frac{\partial F}{\partial P_x}$$

$$= \frac{2\pi}{a+b} (E_x - P_x) \frac{\partial F}{\partial z}$$

where

$$\frac{\partial F}{\partial z} = \frac{1}{2z}(F - e^{-z}), \quad \lim_{z \to 0} F = 1, \quad \lim_{z \to 0} \frac{\partial F}{\partial z} = -\frac{1}{3}.$$

The following integrals are obtained

$$\langle \phi_A | \frac{x}{r_E} | \phi_B \rangle = -P_x G_N + (E_x - P_x) M_N$$

$$\langle \phi_A | \frac{y}{r_E} | \phi_B \rangle = -P_y G_N + (E_y - P_y) M_N$$

$$\langle \phi_A | \frac{z}{r_E} | \phi_B \rangle = -P_z G_N + (E_z - P_z) M_N$$

where

$$G_N = \langle \phi_A | \frac{-1}{r_E} | \phi_B \rangle$$

$$M_N = \frac{-1}{EP^2} \left\{ G_N \left[2(a+b)\right]^{-1} + \pi^{-1/2}(a+b)^{-1/2} e^{-(a+b)EP^2} \langle \phi_A | \phi_B \rangle \right\}$$

In case $EP^2 = 0$, M_N should be replaced by $\lim_{EP^2 \to 0} M_N$.
The final expression for h_z is

$$\langle \phi_A | h_z | \phi_B \rangle = 4ab \left\{ (A_x - B_x) E_y + (B_y - A_y) E_x + B_x A_y - B_y A_x \right\} M_N Z_E$$

Corresponding expressions for h_x and h_y which are derivable from h_z by an appropriate interchange of coordinates are given in Chapter III.

Orbital Angular Momentum

The orbital angular momentum operator

$$r \times p = i(yp_z - zp_y) + j(zp_x - xp_z) + k(xp_y - yp_x)$$

is considered relative to a fixed origin in space. Differentiation gives

$$\int e^{-ar_A^2} \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) e^{-br_B^2} dv = -2b \int (zB_y - yB_z) e^{-(a+b) r_P^2} dv$$

The final integral is easily evaluated from the overlap integral, by differentiation with respect to P_z and P_y as in the spin-orbit derivation. Formulas are given in Chapter III.

Quadrupole Moment

The required integral is

$$\int e^{-ar_A^2} e^{-br_B^2} (3z^2 - r^2) \, dv$$

where the Gaussian functions are defined relative to the fixed origin

of the quadrupole moment operator. It is convenient to translate axes to the point P determined by product of Gaussian functions where $P_x = \frac{aA_x + bB_x}{a+b}$ etc. Thus,

$$x = x_p + P_x, \quad y = y_p + P_y, \quad z = z_p + P_z$$

and the integral becomes

$$e^{-AB^2\frac{ab}{a+b}} \int e^{-(a+b)r_p^2} \left\{ 2(z_p + P_z)^2 - (x_p + P_x)^2 - (y_p + P_y)^2 \right\} dx_p dy_p dz_p$$

The final result given in Chapter III is obtained by direct integration after transformation to spherical coordinates.

Spin-spin Interaction

The spin-spin interaction integral,

$$\int \psi(1,2) \left(\frac{3z_{12}^2 - r_{12}^2}{r_{12}^5} \right) \psi(1,2)\, dv_1 dv_2$$

obtained from the expansion of the general spin-spin interaction Hamiltonian in Chapter IX is evaluated in this section for wavefunctions subject to the restriction

$$\psi(1,2) = 0 \quad \text{if} \quad (x_1, y_1, z_1) = (x_2, y_2, z_2)$$

i.e., the wavefunction vanishes if electrons 1 and 2 have the same coordinates.

The following identities may be verified by differentiation.

$$(3z_{12}^2 - r_{12}^2)\, r_{12}^{-5} = \frac{\partial^2}{\partial z_1^2} \frac{1}{r_{12}}$$

and

$$\psi^2 \frac{\partial^2}{\partial z_1^2} \frac{1}{r_{12}} = \frac{\partial}{\partial z_1}\left(\psi^2 \frac{\partial}{\partial z_1} \frac{1}{r_{12}} - \frac{1}{r_{12}} \frac{\partial}{\partial z_1} \psi^2\right) + \frac{1}{r_{12}} \frac{\partial^2}{\partial z_1^2} \psi^2$$

where the notation for real wavefunctions is used,

Integration gives

$$\int \psi^2 \frac{\partial^2}{\partial z_1^2} \frac{1}{r_{12}}\, dv = \int \frac{\partial}{\partial z_1}\left(\psi^2 \frac{\partial}{\partial z_1} \frac{1}{r_{12}} - \frac{1}{r_{12}} \frac{\partial}{\partial z_1} \psi^2\right) dv + \int \frac{1}{r_{12}} \frac{\partial^2}{\partial z_1^2} \psi^2 dv$$

and

$$\int \frac{\partial}{\partial z_1}\left(\psi^2 \frac{\partial}{\partial z_1} \frac{1}{r_{12}} - \frac{1}{r_{12}} \psi^2\right) dv = -\frac{4\pi}{3} \int P_2(\cos\Theta)\, \psi^2\, \delta(\vec{r}_1 - \vec{r}_2)\, dv_1\, dv_2$$

where the delta function expansion of the integrand given by Pitzer, Kern, and Lipscomb (49) is used. The integral is zero in case $\psi = 0$ when $\vec{r}_1 = \vec{r}_2$, and thus a statement by McWeeny (50) to this effect is verified.

Expansion of ψ as a linear combination of Gaussian functions gives the basic integral

$$\int \frac{1}{r_{12}} \frac{\partial^2}{\partial z_1^2} \left[\phi_A(1)\phi_B(1)\phi_C(2)\phi_D(2)\right] dv = (\text{constant}) \int \frac{Q}{r_{12}} \frac{\partial^2}{\partial z_1^2} R\, dv$$

where the constant is the same as in the simple electron repulsion

integral and

$$Q = \exp\left(-(c+d)\, r_{2Q}^2\right) \qquad R = \exp\left(-(a+b)\, r_{1P}^2\right)$$

Differentiation gives

$$-2(a+b)\int \frac{1}{r_{12}} QR\, dv \;+\; 4(a+b)^2 \int \frac{1}{r_{12}} (z_1 - P_z)^2 QR\, dv$$

The latter integral is evaluated by differentiation of the electron repulsion integral

$$\int \frac{1}{r_{12}} e^{-(a+b) r_{1P}^2 \,-\, (c+d) r_{2Q}^2} dv_1 dv_2$$

with respect to P_z as in the spin-orbit derivation. The result is

$$4(a+b)^2 \int (z - P_z)^2 \frac{1}{r_{12}} RQ\, dv \;=\; 2(a+b) \int \frac{QR}{r_{12}}\, dv + \frac{2\pi^{5/2}}{(a+b)(c+d)(a+b+c+d)^{1/2}} \frac{\partial^2 F(z)}{\partial P_z^2}$$

where $$F(z) = z^{-1/2} \int_0^{z^{1/2}} \exp(-u^2)\, du$$

and $$z = \frac{PQ^2 (a+b)(c+d)}{a+b+c+d}$$

The resulting formula for

$$\int \phi_A(1)\,\phi_B(1)\left(\frac{3z_{12}^2 - r_{12}^2}{r_{12}^5}\right)\phi_C(2)\,\phi_D(2)\,dv$$

is given in Chapter III.

APPENDIX III

COMPUTER PROGRAM FOR THE EVALUATION OF GAUSSIAN FUNCTION INTEGRALS

```
2COMMENT SUBROUTINE SSFUN CALCULATES (1/2),(1/T/2),(1/-1/R/2)
2        1 AND 2 DENOTE 4-TERM LINEAR COMBINATIONS CENTERED AT
2        (X1,Y1,Z1) AND (X2,Y2,Z2) RESPECTIVELY.  THE POTENTIAL
2        FUNCTION (-1/R) IS CENTERED AT (CX,CY,CZ).
2        EXPONENTS COEFFICIENTS     EXPONENTS COEFFICIENTS
2           A1          N1             A2          N2
2           B1          1.0            B2          1.0
2           C1          M1             C2          M2
2           D1          L1             D2          L2                  $
2SUBROUTINE SSFUN                        $
2BEGIN                    $
2SUBROUTINE CALCU                  $
2BEGIN              $
2SUBROUTINE OKP                $
2BEGIN                    $
2        PX=((A.X1)+(B.X2))/(A+B) $  PY=((A.Y1)+(B.Y2))/(A+B)    $
2        PZ=((A.Z1)+(B.Z2))/(A+B)           $
2        CP2 = ((CX-PX)(CX-PX)) + ((CY-PY)(CY-PY)) + ((CZ-PZ)(CZ-PZ))   $
2        X = SQRT(SQRT(A.B))                     $
2        OV = (2.828428.X.X.X/((A+B).SQRT(A+B))).EXP(-A.B.AB2/(A+B))    $
2        KI = (A.B.OV/(A+B))(3.0-(2.0.AB2.A.B/(A+B)))                   $
2        GAUSS = 1.0                        $
2        AA=CP2.(A+B)      $
2        IF CP2 GTR 0.0000001                    $
2BEGIN Y = SQRT(CP2.(A+B))                  $
2        IF Y LEQ 0.8                  $
2BEGIN          $
2        GAUSS = 1.0 + (AA.((-1.0/3.0) + AA.(0.10 + AA.(-0.02380952
2        + AA.(0.004629630 + AA.(-0.0007575758 + AA.(0.0001068376
2        + AA.(-0.00001322751)))))))                      END              $
2        IF Y GTR 0.8                $
2BEGIN                    $
2        IF Y GTR 10.0          $
2        GAUSS=0.8862269/Y        $
2        IF Y LEQ 10.0          $
```

```
2BEGIN  AAA= 1.0 + (Y.(0.0705230784 + Y.(0.0422820123 + Y.(0.0092705272
2        + Y.(0.0001520143 + Y.(0.0002765672 +(0.0000430638.Y)))))))    $
2        DD=AAA.AAA.AAA.AAA          $
2        GAUSS = (0.8862269)(1.0 - (1.0/(DD.DD.DD.DD)))/Y    END          $
2        Y=Y              END         END           $
2        PT = -1.1283792.OV.GAUSS.SQRT(A+B)                               $
2        RETURN END OKP               $
2        B = B2       $
2        ENTER OKP             $
2        OV1=OV $ KI1=KI $ PT1=PT $
2        B=A2 $ ENTER OKP $
2        OV1 = OV1 + (N2.OV)                $
2        KI1 = KI1 + (N2.KI)                $
2        PT1 = PT1 + (N2.PT)                 $
2        B=C2 $ ENTER OKP $
2        OV1 = OV1 + (M2.OV)                  $
2        KI1 = KI1 + (M2.KI)              $
2        PT1 = PT1 + (M2.PT)                $
2        B=D2 $ ENTER OKP $ OV1=OV1+(L2.OV)    $
2        KI1=KI1+(L2.KI) $ PT1=PT1+(L2.PT)    $
2        RETURN END CALCU              $
2        AB2=((X1-X2)(X1-X2))+((Y1-Y2)(Y1-Y2))+((Z1-Z2)(Z1-Z2))          $
2        A=B1 $ ENTER CALCU $ OVL=OV1 $ KIN=KI1 $ PTL=PT1 $
2        A=A1 $ ENTER CALCU $
2        OVL = OVL + (N1.OV1)                 $
2        KIN = KIN + (N1.KI1)                    $
2        PTL = PTL + (N1.PT1)                  $
2        A=C1 $ ENTER CALCU $
2        OVL = (OVL + (M1.OV1))               $
2        KIN = (KIN + (M1.KI1))               $
2        PTL = (PTL + (M1.PT1))                   $
2        A=D1 $ ENTER CALCU $  OVL=OVL + (L1.OV1) $
2        KIN=KIN+(L1.KI1) $ PTL=PTL+(L1.PT1)  $
2        RETURN END SSFUN              $
2        LINEAR COMBINATIONS 1 AND 2 REFER TO ELECTRON 1 AND
```

```
2COMMENT SUBROUTINE SELRP CALCULATES (1,2/ 1/R12 /3,4)
2        LINEAR COMBINATIONS 3 AND 4 REFER ELECTRON 2.   ORIGINS,
2        EXPONENTS, AND COEFFICIENTS ARE DEFINED AS IN SUBROUTINE
2        SSFUN     $
2SUBROUTINE SELRP            $         BEGIN    $
2        CONAB = ((X1-X2)(X1-X2))+((Y1-Y2)(Y1-Y2))+((Z1-Z2)(Z1-Z2))     $
2        CONCD = ((X3-X4)(X3-X4))+((Y3-Y4)(Y3-Y4))+((Z3-Z4)(Z3-Z4))     $
2SUBROUTINE CALC              $ BEGIN  $
2        PX=((A.X1)+(B.X2))/(A+B)                    $
2        PY=((A.Y1)+(B.Y2))/(A+B)              $
2        PZ=((A.Z1)+(B.Z2))/(A+B)                $
2SUBROUTINE REPL         $ BEGIN   $
2        QX=((C.X3)+(D.X4))/(C+D)                $
2        QY=((C.Y3)+(D.Y4))/(C+D)                $
2        QZ=((C.Z3)+(D.Z4))/(C+D)              $
2        RTT = SQRT(SQRT(A.B.C.D))               $
2        Y = SQRT((((PX-QX)(PX-QX)) + ((PY-QY)(PY-QY)) + ((PZ-QZ)(PZ-QZ)
2        ))(A+B)(C+D)/(A+B+C+D))                       $
2        GAUSS = 1.0                  $
2        IF Y GTR 0.0000005                  $      BEGIN    $
2        IF Y LEQ 0.8                 $
2BEGIN   AA = Y.Y                     $
2        GAUSS = 1.0 + (AA.((-1.0/3.0) + AA.(0.10 + AA.(-0.02380952
2        + AA.(0.004629630 + AA.(-0.0007575758 + AA.(0.0001068376
2        + AA.(-0.00001322751)))))))                          END                $
2        IF Y GTR 0.8                 $          BEGIN  $
2        IF Y GTR 10.0           $
2        GAUSS=0.8862269/Y          $
2        IF Y LEQ 10.0           $
2BEGIN  AA = 1.0 + (Y.(0.0705230784 + Y.(0.0422820123 + Y.(0.0092705272
2        + Y.(0.0001520143 + Y.(0.0002765672 +(0.0000430638.Y)))))))    $
2        DD = AA.AA.AA.AA                 $
2        GAUSS = (0.8862269)(1.0 - (1.0/(DD.DD.DD.DD)))/Y    END          $
2        Y=Y              END          END            $
2      RES=(((9.0270336).GAUSS/((A+B)(C+D).SQRT(A+B+C+D))).EXP(-(CONAB.
```

```
2         A.B/(A+B))-(CONCD.C.D/(C+D)))).RTT.RTT.RTT                          $
2         RETURN END REPL                                                    $
2         C=B3 $ D=B4 $ ENTER REPL $ P=RES $ D=C4 $ ENTER REPL $
2         P=P+(M4.RES) $ D=A4 $ ENTER REPL $ P=P+(N4.RES) $
2         D=D4 $ ENTER REPL $ P=P+(L4.RES)  $
2         C=C3 $ D=B4  $
2         ENTER REPL $ P=P+(M3.RES) $ D=C4 $ ENTER REPL $
2         P=P+(M3.M4.RES) $ D=A4 $ ENTER REPL $ P=P+(M3.N4.RES) $
2         D=D4 $ ENTER REPL $ P=P+(M3.L4.RES)  $
2         C=A3 $ D=B4 $ ENTER REPL $ P=P+(N3.RES) $ D=C4 $ ENTER REPL $
2         P=P+(N3.M4.RES) $ D=A4 $ ENTER REPL $ P=P+(N3.N4.RES) $
2         D=D4 $ ENTER REPL $ P=P+(N3.L4.RES)  $
2         C=D3 $ D=B4 $ ENTER REPL $ P=P+(L3.RES) $
2         D=C4 $ ENTER REPL $ P=P+(L3.M4.RES)  $
2         D=A4 $ ENTER REPL $ P=P+(L3.N4.RES)  $
2         D=D4 $ ENTER REPL $ P=P+(L3.L4.RES)  $
2         RESU=P $ RETURN END CALC $
2         A=B1 $ B=B2 $ ENTER CALC $ RESUL=RESU $ B=C2 $ ENTER CALC $
2         RESUL = RESUL+(M2.RESU) $ B=A2 $
2         IF N2 GTR 0.0000005 $ ENTER CALC $ RESUL=RESUL+(N2.RESU)  $
2        B=D2 $ IF L2 GTR 0.0000005 $ ENTER CALC $ RESUL=RESUL+(L2.RESU)$
2         A=C1 $ B=B2 $ ENTER CALC $ RESUL=RESUL+(M1.RESU) $ B=C2 $
2         ENTER CALC $ RESUL=RESUL+(M1.M2.RESU) $ B=A2 $
2         IF N2 GTR 0.0000005 $ ENTER CALC$ RESUL=RESUL+(M1.N2.RESU) $
2    B=D2 $ IF L2 GTR 0.0000005 $ ENTER CALC $ RESUL=RESUL+(M1.L2.RESU) $
2         A=A1 $ B=B2 $ IF N1 GTR 0.0000005 $ ENTER CALC $
2         RESUL = RESUL+(N1.RESU) $ B=C2 $
2         IF N1 GTR 0.0000005 $ ENTER CALC $
2         RESUL=RESUL+(N1.M2.RESU) $ B=A2 $
2         IF (N1.N2) GTR 0.0000005 $ ENTER CALC $
2         RESUL=RESUL+(N1.N2.RESU) $
2    B=D2 $ IF L2 GTR 0.0000005 $ ENTER CALC $ RESUL=RESUL+(N1.L2.RESU) $
2         A=D1   $
2    B=B2 $ IF L1 GTR 0.0000005 $ ENTER CALC $ RESUL=RESUL+(L1.RESU)    $
2    B=C2 $ IF L1 GTR 0.0000005 $ ENTER CALC $ RESUL=RESUL+(L1.M2.RESU) $
```

```
2    B=A2 $ IF L1 GTR 0.0000005 $ ENTER CALC $ RESUL=RESUL+(L1.N2.RESU) $
2         B=D2  $
2      IF (L1.L2) GTR 0.0000005 $ ENTER CALC $ RESUL=RESUL+(L1.L2.RESU) $
2         REP = RESUL       $
2         RETURN END SELRP     $
2         X1=X2=Y1=Y2=Z1=Z2=CX=CY=CZ=0.0 $
2         A2=A1=0.139452 $ N2=N1=6.7 $
2         B2=B1=2.83994 $
2         C2=C1=0.578897 $ M2=M1=4.9 $
2         D2=D1=17.499 $ L2=L1=0.156 $
2         ENTER SSFUN $ OVER=OVL $ KINE=KIN/OVL $ POTEN=PTL/OVL $
2         A3=A4=A1 $ N3=N4=N1 $
2         B3=B4=B1 $
2         C3=C4=C1 $ M3=M4=M1 $
2         D3=D4=D1 $ L3=L4=L1 $
2         X3=X4=Y3=Y4=Z3=Z4=0.0 $
2         ENTER SELRP $ EREP=REP/(OVL.OVL) $
2         WRITE ($$ANS,FANS)     $
2         READ ($$ANY) $
2INPUT ANY(THING) $
2OUTPUT ANS(OVER,KINE,POTEN,EREP) $
2FORMAT FANS(B1,4X20.8,W0) $
2         FINISH     $
```

APPENDIX IV

SPIN-ORBIT AND ORBITAL ANGULAR MOMENTUM MATRIX ELEMENTS

Spin-Orbit[a]

		h'_x[b]	h'_y	h'_z
$\langle q_1 \vert h \vert p_1^o \rangle$	O1[c]	2.94251	-1.69886	0.0
	C1	0.07369	-0.04254	0.0
	C2	0.00170	-0.01074	0.0
	O2	0.00167	-0.00329	0.0
$\langle q_1 \vert h \vert p_1^c \rangle$	O1	0.13965	-0.08063	0.0
	C1	0.06431	-0.03713	0.0
	C2	0.00167	-0.00542	0.0
	O2	0.00025	-0.00139	0.0
$\langle q_1 \vert h \vert p_2^c \rangle$	O1	0.00545	-0.00315	0.0
	C1	0.00133	-0.00510	0.0
	C2	-0.00332	-0.00244	0.0
	O2	-0.00056	-0.00061	0.0
$\langle q_1 \vert h \vert p_2^o \rangle$	O1	0.00000	0.00000	0.0
	C1	0.00000	-0.00001	0.0
	C2	-0.00003	-0.00002	0.0
	O2	0.00000	-0.00000	0.0
$\langle q_1 \vert h \vert p_b \rangle$[d]	O1	0.0	0.0	-3.39771
	C1	0.0	0.0	0.04030
	C2	0.0	0.0	0.00617
	O2	0.0	0.0	0.00195

Orbital Angular Momentum[a]

	M'^{e}_x	M'_y	M'_z
$\langle q_1 \lvert M \rvert p_1^o \rangle$	0.86601	-0.50000	0.0
$\langle q_1 \lvert M \rvert p_1^c \rangle$	0.19928	-0.11506	0.0
$\langle q_1 \lvert M \rvert p_2^c \rangle$	-0.01982	-0.03529	0.0
$\langle q_1 \lvert M \rvert p_2^o \rangle$	-0.00035	-0.00005	0.0
$\langle q_1 \lvert M \rvert p_b \rangle$	0.0	0.0	-1.0000

a. Additional integrals over atomic orbitals are given in a supplement to this thesis (66).

b. Spin-orbit interaction operators are defined relative to the symmetry axes shown in Figure 4 of Chapter VII;

$h'_x = \frac{\partial v}{\partial y}\frac{\partial}{\partial z} - \frac{\partial v}{\partial z}\frac{\partial}{\partial y}$, etc., where $v = 1/r_k$. Numerical values are in atomic units.

c. The notation indicates the origin of the potential function; $v = 1/r_k$ k = O1, C1, C2, O2, where the labels refer to oxygen and carbon nuclei 1 and 2 in Figure 4.

d. The function p_b is a 2p orbital in the same direction as s_1^s in Figure 4.

e. Orbital angular momentum operators are defined relative to the symmetry axes shown in Figure 4.

APPENDIX V

PERTURBATION THEORY FOR DEGENERATE SYSTEMS

General Theory

The influence of higher energy states in the perturbation of a set of degenerate or near degenerate states is considered in this appendix. Solutions to an unperturbed problem,

$$H_0\Phi^0 = E_0\Phi^0$$

are assumed known, and for the example case treated here, are taken as the orthogonal set

$$\Phi_1^0, \Phi_2^0, \cdots, \Phi_k^0, \cdots$$

with corresponding eigenvalues,

$$E_1^0, E_2^0, \cdots, E_k^0, \cdots$$

where

$$E_1^0 = E_2^0 = E_3^0 << E_k^0 \quad k = 4,5,\cdots$$

That is, three of the levels are assumed degenerate, and also widely separated from the remaining levels. More general cases may be treated in exactly the same manner as this example case.

The problem of real interest in this work is one in which H_o is slightly modified by a perturbation H'. Solutions of this eigenvalue problem,

$$(H_o + H')\Phi_k = E_k \Phi_k$$

may be expanded as linear combinations of the assumed complete set to give

$$\Phi_k = \sum_l c_l \Phi_l^o$$

In nondegenerate applications the more explicit statement,

$$\Phi_k = N^{-1}\left\{\Phi_k^o + \lambda \Phi^{(1)} + \lambda^2 \Phi^{(2)} + \cdots\right\}$$

is possible where $\Phi^{(1)}$ and $\Phi^{(2)}$ are linear combinations of $\{\Phi_l^o\}$ and λ is related to the magnitude of the perturbation. Thus, Φ_k approaches Φ_k^o as the perturbation vanishes. In degenerate problems, however, the solution in the limit of vanishing perturbation is not known, and for example, is determined only to the extent

$$\Phi_1 = N^{-1}\left\{c_1 \Phi_1^o + c_2 \Phi_2^o + c_3 \Phi_3^o\right\}$$

and similarly for Φ_2 and Φ_3, subject to orthogonality restrictions. It is not possible to specify the linear combination in more detail, regardless of what is known about the unperturbed system, e.g., in a

triplet system in which the spin operators S^2 and S_z commute with the unperturbed Hamiltonian, solutions must be the eigenfunctions of S^2 and S_z,

$$\Phi_T\,\alpha(1)\,\alpha(2) \qquad \Phi_T\,\frac{\alpha(1)\beta(2)+\alpha(2)\beta(1)}{\sqrt{2}} \qquad \Phi_T\,\beta(1)\beta(2)$$

for a two electron system. It is not possible, however, to conclude that any <u>one</u> of these functions is the correct solution in the limit of vanishing perturbation; this statement is equivalent to the statement that there is no unique direction of z in the description of the unperturbed system.

A direct variational determination of the expansion coefficients

$$\Phi_k = \sum_l c_l \Phi_l^\circ$$

is of course possible in principle, but in practice may be ruled out if a large number of states is involved.

Instead of using the basis, $\{\Phi_l^\circ\}$, directly, consider the following unitary transformations.

$$\begin{pmatrix} \Phi_1' \\ \Phi_2' \\ \Phi_3' \\ \Phi_4' \\ \vdots \end{pmatrix} = N^{-1} U_1 U_2 U_3 \cdots \begin{pmatrix} \Phi_1^\circ \\ \Phi_2^\circ \\ \Phi_3^\circ \\ \Phi_4^\circ \\ \vdots \end{pmatrix}$$

where U_3 is diagonal except for the elements $\lambda_{14}, \lambda_{15}, \lambda_{16}, \cdots$, and $\lambda_{41}, \lambda_{51}, \lambda_{61}, \cdots$; thus,

$$U_3 = N_3^{-1} \begin{pmatrix} 1 & 0 & 0 & \lambda_{14} & \lambda_{15} & \lambda_{16} & \\ 0 & 1 & 0 & 0 & 0 & 0 & \\ 0 & 0 & 1 & 0 & 0 & 0 & \\ \lambda_{41} & 0 & 0 & 1 & 0 & 0 & \vdots \\ \lambda_{51} & 0 & 0 & 0 & 1 & 0 & \\ \lambda_{61} & 0 & 0 & 0 & 0 & 1 & \\ & & & \cdots & & & \end{pmatrix}$$

and $\lambda_{41} = -\lambda_{14}^*$, $\lambda_{51} = -\lambda_{15}^*$, $\lambda_{61} = -\lambda_{16}^*$ etc. The other matrices similarly are diagonal except for elements in the second row and column and third row and column, respectively, i.e.,

$$U_2 = N_2^{-1} \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & \\ 0 & 1 & 0 & \lambda_{24} & \lambda_{25} & \lambda_{26} & \\ 0 & 0 & 1 & 0 & 0 & 0 & \\ 0 & \lambda_{42} & 0 & 1 & 0 & 0 & \vdots \\ 0 & \lambda_{52} & 0 & 0 & 1 & 0 & \\ 0 & \lambda_{62} & 0 & 0 & 0 & 1 & \\ & & & \cdots & & & \end{pmatrix}$$

$$U_1 = N_1^{-1} \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & \\ 0 & 1 & 0 & 0 & 0 & 0 & \\ 0 & 0 & 1 & \lambda_{34} & \lambda_{35} & \lambda_{36} & \\ 0 & 0 & \lambda_{43} & 1 & 0 & 0 & \vdots \\ 0 & 0 & \lambda_{53} & 0 & 1 & 0 & \\ 0 & 0 & \lambda_{63} & 0 & 0 & 1 & \\ & & & \cdots & & & \end{pmatrix}$$

Thus, omitting normalizations, the following equivalent set is obtained.

$$\Phi_1' = \Phi_1 + \lambda_{14}\Phi_4 + \lambda_{15}\Phi_5 + \cdots$$

$$\Phi_2' = \Phi_2 + \lambda_{24}\Phi_4 + \lambda_{25}\Phi_5 + \cdots + \lambda_{41}\lambda_{24}\Phi_1$$

$$\Phi_3' = \Phi_3 + \lambda_{34}\Phi_4 + \lambda_{35}\Phi_5 + \cdots + \lambda_{42}\lambda_{34}\Phi_2 + \lambda_{41}\lambda_{34}\Phi_1$$

$$\Phi_4' = \Phi_4 + \lambda_{42}\Phi_2 + \lambda_{41}\Phi_1 + \lambda_{43}\Phi_3 + \cdots$$

$$\cdots$$

If matrix elements, λ , are chosen as the coefficients that appear in the usual nondegenerate perturbation theory, and if terms of an order greater than or equal to λ^2 are omitted, the functions become

$$\Phi_1' = \Phi_1^\circ + \sum''' \frac{H_{k1}'}{E_1 - E_k}\Phi_k^\circ$$

$$\cdots$$

$$\Phi_4' = \Phi_4^\circ - \sum_{k=1}^{3} \frac{H_{k4}'}{E_k - E_4}\Phi_k^\circ$$

$$\cdots$$

where the triple prime denotes summation over all functions Φ_k, $k \geq 4$. The functions, therefore, are the ones obtained in nondegenerate theory if all mixings of degenerate states are excluded.

The important accomplishment of the transformation is a reduction in magnitude of the interaction with higher energy states. The original interaction between Φ_1° and Φ_4° was of magnitude,

$$\langle \phi_1^\circ \mid H_\circ + H' \mid \phi_4^\circ \rangle \quad = \quad \langle \phi_1^\circ \mid H' \mid \phi_4^\circ \rangle \quad = \quad H_{14}'$$

but after transformation becomes

$$\langle \phi_1' \mid H_\circ + H' \mid \phi_4' \rangle \approx \frac{H_{14}'}{E_1 - E_4} \left\{ \frac{|H_{14}'|^2}{E_1 - E_4} + \frac{|H_{24}'|^2}{E_2 - E_4} + \frac{|H_{34}'|^2}{E_3 - E_4} \right\}$$

Similar results are obtained for ϕ_2, ϕ_3, ϕ_5 etc.

Therefore, in a treatment of the initially degenerate states, the functions ϕ_4', ϕ_5' etc. may be neglected to a good approximation, and only the functions ϕ_1', ϕ_2', and ϕ_3' retained as a basis. Energy minimization of the linear combination

$$\psi = \sum_{k=1}^{3} c_k \phi_k'$$

leads to the usual set of secular equations and corresponding determinant condition

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & H_{13} - ES_{13} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & H_{23} - ES_{23} \\ H_{31} - ES_{31} & H_{32} - ES_{32} & H_{33} - ES_{33} \end{vmatrix} = 0$$

where

$$H_{ij} = \langle \phi_i' | H_o + H' | \phi_j' \rangle$$

$$S_{ij} = \langle \phi_i' | \phi_j' \rangle$$

and E is the energy eigenvalue. Substitution of the approximate value for E,

$$E \approx E_1^\circ = E_2^\circ = E_3^\circ$$

in the off-diagonal terms followed by an expansion of matrix elements gives the result,

$$0 = \begin{vmatrix} H_{11} - E - \sum''' \frac{|H'_{1k}|^2}{E_k - E_1} & H_{12} - \sum''' \frac{H'_{1k} H'_{k2}}{E_k - E_1} & H_{13} - \sum''' \frac{H'_{1k} H'_{k3}}{E_k - E_1} \\ \text{——} & H_{22} - E - \sum''' \frac{|H'_{2k}|^2}{E_k - E_1} & H_{23} - \sum''' \frac{H'_{2k} H'_{k3}}{E_k - E_1} \\ \text{——} & \text{——} & H_{33} - E - \sum''' \frac{|H'_{3k}|^2}{E_k - E_1} \end{vmatrix}$$

The effect of higher energy states on initially degenerate states thus has been well approximated.

Electronic Transitions to Degenerate Triplet States

The calculation of singlet-triplet transition probabilities in Chapter VIII is based on a spin-orbit mixing of the three triplet components with higher energy singlet states. Certain conclusions of the previous section permit a simple expression of the results. The initially degenerate triplet functions Φ_1°, Φ_2°, and Φ_3°, corresponding to the eigenvalues 0 and ±1 of S_z, are mixed with singlet functions, Φ_4°, Φ_5°, etc., by the spin-orbit perturbation H' to give the new basis,

$$\Phi_1' = \Phi_1^\circ + \sum_{k\geq 4} \lambda_{1k}\Phi_k^\circ$$

$$\Phi_2' = \Phi_2^\circ + \sum_{k\geq 4} \lambda_{2k}\Phi_k^\circ$$

$$\Phi_3' = \Phi_3^\circ + \sum_{k\geq 4} \lambda_{3k}\Phi_k^\circ$$

The functions, Φ', are not correct wavefunctions for electronic states, but instead are only basis functions to be used in a variational treatment. The proper electronic functions obtained by a variational solution are related to Φ_1', Φ_2', and Φ_3' by the transformation

$$\begin{pmatrix} \Phi_1'' \\ \Phi_2'' \\ \Phi_3'' \end{pmatrix} = \begin{pmatrix} C_{11} & C_{12} & C_{13} \\ C_{21} & C_{22} & C_{23} \\ C_{31} & C_{32} & C_{33} \end{pmatrix} \begin{pmatrix} \Phi_1' \\ \Phi_2' \\ \Phi_3' \end{pmatrix}$$

In the following derivation the transformation is assumed unitary although this is only approximately correct since the functions Φ' are orthogonal only to the order λ^2.

The probability, $P_{T \leftarrow S}$, of a transition from a singlet state S, to the triplet state T, is equal to the sum of transition probabilities to each component function Φ_1'', Φ_2'', and Φ_3''. Thus,

$$P_{T \leftarrow S} = P_{1 \leftarrow S} + P_{2 \leftarrow S} + P_{3 \leftarrow S}$$

$$= \left| c_{11} \langle \Phi_S | R | \Phi_1' \rangle + c_{12} \langle \Phi_S | R | \Phi_2' \rangle + c_{13} \langle \Phi_S | R | \Phi_3' \rangle \right|^2$$

$$+ \left| c_{21} \langle \Phi_S | R | \Phi_1' \rangle + c_{22} \langle \Phi_S | R | \Phi_2' \rangle + c_{23} \langle \Phi_S | R | \Phi_3' \rangle \right|^2$$

$$+ \left| c_{31} \langle \Phi_S | R | \Phi_1' \rangle + c_{32} \langle \Phi_S | R | \Phi_2' \rangle + c_{33} \langle \Phi_S | R | \Phi_3' \rangle \right|^2$$

where R denotes the transition moment operator corresponding to an electric dipole, magnetic dipole, or quadrupole mechanism. Expansion of the squared magnitudes using the unitary property of the matrix (c_{ij}) gives

$$P_{T \leftarrow S} = |\langle \Phi_S | R | \Phi_1' \rangle|^2 + |\langle \Phi_S | R | \Phi_2' \rangle|^2 + |\langle \Phi_S | R | \Phi_3' \rangle|^2$$

which proves that the correct transition probability would be calculated if the functions Φ_1', Φ_2', and Φ_3' were assumed to be the proper electronic state functions in the presence of a spin-orbit perturbation. In fact, however, the functions Φ_1'', Φ_2'', and Φ_3'' are the correct solutions.

APPENDIX VI

NITROGEN MOLECULE ELECTRON REPULSION INTEGRALS

(11,11) =	2.3360137	(11,33) =	2.3360137
(11,55) =	0.6650371	(11,99) =	0.6995643
(11,1111) =	0.7332068	(11,1313) =	0.709893
(13,31) =	1.852701	(15,51) =	0.0062345
(19,91) =	0.0251502	(111,111) =	0.0220203
(113,131) =	0.007821	(33,33) =	2.3360137
(33,55) =	0.6650371	(33,99) =	0.6995640
(33,1111) =	0.7332065	(33,1313) =	0.709893
(35,53) =	0.006025	(39,93) =	0.0251605
(311,113) =	0.0220159	(313,133) =	0.0073229
(55,55) =	0.576975	(55,77) =	0.526530
(55,99) =	0.5292076	(55,1111) =	0.5714021
(55,1313) =	0.540105	(57,75) =	0.0237644
(59,95) =	0.0594409	(511,115) =	0.1055034
(513,135) =	0.0275431	(99,99) =	0.5507437
(99,1111) =	0.5521468	(99,1313) =	0.491947
(911,119) =	0.1571573	(913,139) =	0.09742
(1111,1111) =	0.6051427	(1111,1313) =	0.585119
(1113,1311) =	0.10415	(1313,1313) =	0.62149

---

a. Notation: $(ab,cd) = (\varphi_a(1)\ \varphi_b(1)|\frac{1}{r_{12}}|\ \varphi_c(2)\ \varphi_d(2))$ where the functions, φ, are molecular orbitals defined in Chapter IV.

APPENDIX VII

MATRIX ELEMENTS OF DETERMINANTAL WAVEFUNCTIONS

In this appendix the matrix element of a one-electron operator Γ and two determinantal wavefunctions ψ_1 and ψ_2 is evaluated. The result is well known and is given for example by Eyring, Walter, and Kimball (32), but for purposes of completeness in the treatment of spin-orbit interaction, a proof is given here.

Consider the two functions

$$\psi_1 = (N!)^{-1/2} \det \left(\phi_{i_1}(1)\, \bar{\phi}_{i_1}(2)\, \phi_{i_2}(3)\, \bar{\phi}_{i_2}(4) \cdots \phi_n(2n-1)\, \bar{\phi}_n(2n)\, \bar{\bar{\phi}}_{j_3}(2n+1)\, \bar{\bar{\phi}}_{j_p}(2n+2) \right)$$

$$\psi_2 = (N!)^{-1/2} \det \left(\phi_{i_1}(1)\, \bar{\phi}_{i_1}(2)\, \phi_{i_2}(3)\, \bar{\phi}_{i_2}(4) \cdots \phi_n(2n-1)\, \bar{\phi}_n(2n)\, \bar{\bar{\phi}}_{j_q}(2n+1)\, \bar{\bar{\phi}}_{j_r}(2n+2) \right)$$

where the ϕ_k are orthonormal molecular orbitals, and the implied meaning of the bar notation is

$$\phi_{i_1}(1) \sim \phi_{i_1}(1)\alpha(1)$$

$$\bar{\phi}_{i_1}(1) \sim \phi_{i_1}(1)\beta(1)$$

The spin of the double bar functions is not specified. The matrix element

$$\langle \psi_1 | \Gamma | \psi_2 \rangle$$

where

$$\Gamma = \sum_k^{2n+2} \Gamma_k$$

may be expanded without loss of generality to give

$$(N!)(N!)^{-1}\langle \det(\phi_1(1)\bar{\phi}_1(2)\cdots \bar{\phi}_s(2n+1)\bar{\phi}_p(2n+2)|\Gamma|\phi_1(1)\bar{\phi}_1(2)\cdots\bar{\phi}_q(2n+1)\bar{\phi}_r(2n+2)\rangle$$

in which the diagonal element of the second determinant represents all N! products. Only one of the possible N! products of the first determinant gives a nonvanishing contribution, and in this case the electron labels must be matched exactly with the electron labels of the right-hand product. If q and r are different from both s and p, the orthogonality of orbital or spin functions causes the matrix element to vanish. Thus one of the functions q or r must agree with s or p and if q = s the matrix element has the value

$$\langle \bar{\phi}_p(1)|\Gamma_1|\bar{\phi}_r(1)\rangle$$

which is the well-known result for a one-electron operator.

The important consequence of this slightly less than general proof is that only the open shell configuration needs to be considered in an evaluation of one-electron matrix elements, and thus it is possible to write triplet functions as

$$\Psi_1 = 2^{-1/2}\{\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)\}\alpha(1)\alpha(2)$$

$$\Psi_0 = 2^{-1}\{\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)\}\{\alpha(1)\beta(2) + \alpha(2)\beta(1)\}$$

$$\Psi_{-1} = 2^{-1/2}\{\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)\}\beta(1)\beta(2)$$

instead of using a complete determinant wavefunction. The same result applies for a singlet function.

APPENDIX VIII

FINE STRUCTURE ENERGY LEVELS IN THE TRIPLET STATE OF GLYOXAL

The fine structure energy levels of glyoxal given on the following page were calculated using the formula

$$E = \langle NK | H | NK \rangle = \tfrac{1}{2}(A+B)[N(N+1)] + [C - \tfrac{1}{2}(A+B)]K^2$$

$$+ \tfrac{1}{2}(a_o - a)R + \frac{3aK^2}{N(N+1)} + (3K^2 - N(N+1))\alpha\rho$$

where

$$R = N(N+1) - J(J+1) + 2$$

$$\rho = \frac{3R(R-1) - 8N(N+1)}{2N(N+1)(2N-1)(2N+3)}$$

and

$$A = B = 0.158$$

$$C = 1.9$$

$$\alpha = 0.26$$

$$a_o = 0.0028$$

$$a = 0.0014$$

The constants a_o and a obtained in Chapter IX differ slightly from the above values.

K	N	E $\alpha = a_o = a = o$	J	$E(cm^{-1})$ $\alpha = 0.26$ $a_o = a = o$	$E(cm^{-1})$
1	1	2.058	0	2.318	2.325
			1	1.928	1.932
			2	2.084	2.081
1	2	2.690	1	2.560	2.566
			2	2.820	2.822
			3	2.653	2.649
1	3	3.638	2	3.482	3.489
			3	3.833	3.835
			4	3.573	3.568
2	2	7.916	1	8.176	8.189
			2	7.656	7.660
			3	7.990	7.982
2	3	8.864	2	8.864	8.875
			3	8.864	8.867
			4	8.864	8.856
2	4	10.128	3	10.054	10.065
			4	10.232	10.234
			5	10.090	10.081
4	4	31.032	3	31.292	31.316
			4	30.668	30.673
			5	31.164	31.145
4	5	32.612	4	32.716	32.738
			5	32.456	32.460
			6	32.672	32.654

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